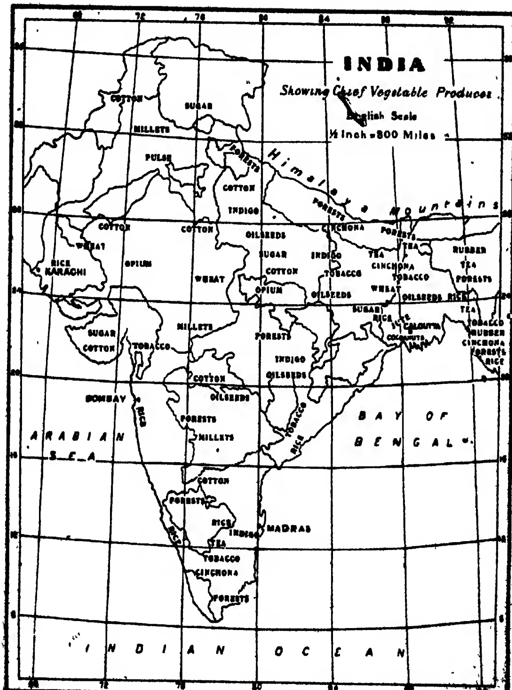
MODERN CHEMISTRY AND CHEMICAL INDUSTRY OF STARCH AND CELLULOSE


INDIA
Showing Chief Vegetable Produces
English Scale
½ Inch = 800 Miles
Himalaya Mountains
COTTON
SUGAR
MILLETS
PULSE
FORESTS
INDIGO
OILSEEDS
CINCHONA
TEA
RUBBER
WHEAT
RICE
KARACHI
OPIUM
TOBACCO
CALCUTTA
COCOANUTS
BOMBAY
MADRAS
ARABIAN SEA
BAY OF BENGAL
INDIAN OCEAN

MODERN CHEMISTRY AND CHEMICAL INDUSTRY OF STARCH AND CELLULOSE

(*WITH REFERENCE TO INDIA*)

BY

TARINI CHARAN CHAUDHURI, M.A.

Professor of Chemistry, Krisnath College, Berhampore (Bengal); Formerly Government Research Scholar in Chemistry; Author of "Sir William Ramsay as a Scientist and Man," etc.

ALCUTTA:

BUTTERWORTH & CO. (INDIA), LTD., 6, HASTINGS ST.

WINNIPEG:
BUTTERWORTH & CO. (Canada), Ltd

SYDNEY:
BUTTERWORTH & Co. (Australia), Ltd.

LONDON:

BUTTERWORTH & CO., BELL YARD, TEMPLE BAR.

Medical Publishers

1918

PRINTED BY
D. N. DE, AT THE SWARNA PRESS, 107, MECHUABAZAR ST., PAGES 1 TO 156;
AND THE REST BY CALEDONIAN PRINTING CO., LTD., CALCUTTA.

PREFACE

THE subject of starch and cellulose is indeed so vast that it may be said to cover, when considered in all its remote aspects, practically the whole domain of organo-chemical technology. Each particular branch of the subject would eminently supply materials for individual volumes; this is, however, not within the scope of the present work. While engaged in the study of starch and cellulose, the writer felt the necessity for a handy compendium on the subject containing up-to-date information in all its bearings. Although there is no dearth of ably written text-books or technical works in the field of organic chemistry, monographs, based on original sources, have a special value of their own. With this end in view, it has been attempted, in the present volume, to give a brief survey of the chemistry and the various chemical industries that have direct and indirect bearing on starch and cellulose, specially in the light of recent researches—theoretical and technological.

The book is accordingly divided into two parts, theoretical and industrial. The first deals with the general position of the composition of starch and cellulose from analytic and synthetic stand-

points, whilst the second gives an outline of their manifold technical applications, occasionally with reference to their industrial possibilities in India. Attempt has also been made to incidentally point out the modern lines of movement of these branches of chemistry where there is room for further studies and industrial expansion. Each of the more important branches of the subject has been treated historically according to the gradual process of evolution. Except in the case of well-known facts, references to important original literature and other sources of information have been given. For all suggestions, observations and criticisms, not otherwise acknowledged, the author himself is mainly responsible.

It has been found by experience that during the general college-course, attention of the student is focussed literally on starch and cellulose themselves. It is hoped that the many-sided techno-chemical rôle played by these two substances in the numerous arts and industries, briefly described in this small volume, will serve to widen the outlook of the chemical reader.

Besides referring to many Journals published by various scientific societies of the world, patent literature and standard works, I have consulted many English, American and German authorities and also publications of other countries, to the authors and the publishers of which my

best thanks are due. I am indebted to Dr. E. R. Watson, M.A., D.Sc., from whom I received my first inspiration to study the present subject industrially, and also to Dr. P. Neogi, M.A., Ph.D., Prof. A. Maitra, M.A. and Mr. B. Adicari, M.A., for their friendly criticisms and suggestions; to all of them I offer my grateful thanks.

H. F. PRESERVING CO.,
MALDA, INDIA,
April, 1918.

T. C. C.

CONTENTS

MODERN CHEMISTRY

AND

CHEMICAL INDUSTRY

OF

STARCH AND CELLULOSE.

CHAPTER I.

Primary Uses and Nomenclature of Starch and Cellulose.

1. The scope of the subject.—The subject for the present discourse—"Starch and Cellulose with special reference to their applications in modern industries"*—is an extensive one ; and to do full justice to all the branches of

* Original title of a lecture delivered before the Rajshahi Government College Union, Jan. 19, 1915.

industries, having direct or indirect bearing on starch and cellulose, would go to make volumes. In the present paper, however, only the main outlines of the subject will be dealt with, treating the important ones more fully and, to some extent, incidentally emphasising the industrial possibilities in India.

2. Gradual introduction of textile fibres: jute and cotton in India. *—Starch and cellulose are substances essentially of vegetable origin. From very ancient times of which we have any record, man came to wear barks of trees, and these barks are nothing but a crude form of ligno-cellulose. With the onward march of time and progress of mankind, fine cellulose-fibres have been made from the barks of plants ; almost all men in Bengal are familiar with the processes of manufacturing flax or jute fibres. Cotton, though not so largely grown in India, has been in use from very olden times for making fine threads out of which nice hand-made cloths and other textures are woven. The reminiscences of this important Cottage Industry are still to be witnessed in the villages of Bengal. The people of this

* Refer to the Map of India attached to this book for jute and cotton areas.

country are very well familiar with jute for the sake of the pecuniary advantage they draw from its cultivation, and in sympathy, with its adjutant malaria * which is a dear friend to all in the malaria-zone of Bengal.

3. Supremacy of India's valuable textile industry dates from pre-historic times.—Cotton, jute, flax and linen are the most important varieties of cellulose from which fine tough threads are spun with which clothing materials are manufactured, excepting those only that are made of wool and silk which are substances of animal origin. India has been the most famous wool and silk-producing country; and her huge export of these commodities to the western countries from the borders of the Persian gulf to distant Portugal and England as well as to China and the islands of the Malay Archipelago, is well known to all. Indeed India's trade dates from pre-historic times ; and evidences, both *internal* that is, from Indian Literature and other Indian sources, and *external*, that is, from those foreign

* This is due mainly to two-fold causes with respect to jute-cultivation :—(*a*) People often drink the jute-rotten waters in the jute-growing areas ; and (*b*) the stagnant waters, which have generally a dirty bluish or greenish colour and emanate a foul smell, are good mosquito-producing beds.

countries into which the articles were imported, are numerous to justify the statement. All kinds of Sanskrit Literature,—such as the Vedas, the Epics, the Sutras, the Puranas, the Poetical works, Drama and Romance, are replete with references to the ancient maritime trade of India; and there is conclusive proof* 'that the ocean—the highway of modern commerce—was more or less freely used in ancient times by the Indians as the great highway of international trade. These evidences from the Sanskrit Literature are again confirmed by those furnished by the Budhistic

---

* (*a*) India as the Heart of the Old World: Her abounding International Commercial Life.

I. Evidences from Sanskrit Literature:

The Dawn and the Dawn Society's Magazine, Vol. XII, 1909, No. 3, pp. 45-52.

II. Evidences from Budhistic Literature:

The Dawn and the Dawn Society's Magazine, Vol. XII, 1909, No. 4, pp. 57-62.

(*b*) Maritime Activity and Enterprise in Ancient India: Intercourse and Trade by Sea with China.

The Dawn and Dawn Society's Magazine, Vol. XIII, 1910,

Nos. 5-8; Vol. XIV, 1911, Nos. 2 and 5; Vol. XV, 1912, Nos. 2 and 3.

(*c*) Ship-building and Maritime Activity in Bengal.

The Dawn and Dawn Society's Magazine, Vol. XIII, 1910, Nos. 9 and 10; Vol. XIV, 1911, Nos. 1, 4, 8 and 9; Vol. XV, 1912, Nos. 9—12.

(*d*) R. Mukerji, A History of Shipping and Maritime Activity in Ancient India.

Literature, such as the Ceylonese chronicles, the Jatakas, the Greek Literature and so forth.

The mention of hand-made Indian textures may sound to the reader to be a crude form of manufacture ; but leaving alone the bright past of Indian wool and silk articles, a later time produced the famous *muslin* of Dacca,—a cotton fabric—the excellence of which will be written in letters of gold in the pages of an Industrial History of India. The manufacture of this renowned *muslin* is, to the great misfortune of India, in a moribund condition at the present day ; and there seems to be no pulsation for its revival. Attention should now be given to growing more cotton in India, not with a view to export the raw material, but for making textures in sufficient quantities to meet the demand of her people ; and also for the various other industrial uses to which it may profitably be put.

4. Distinction between natural uses and industrial applications of starch and cellulose.—As cellulose gives our clothing, starch is the food on which we live ; as familiar forms of starch may be mentioned rice which is proverbially the principal foodstuff in Bengal, wheat, barley and potato. The tremendous services of starch and cellulose to the whole

human race on the surface of the earth may be only very imperfectly imagined if it is considered that all people are fed and clothed by these two substances in some form or other. These two most important uses of starch and cellulose may be called their *natural or primary uses* in contradistinction to their *artificial or*, more properly, *industrial applications.*

5. Nomenclature of starch and cellulose.—The nomenclature of starch and cellulose is in a very unsatisfactory condition, as the purely chemical studies of the subject have made but little advance. It is extremely difficult to determine the individual homogeneity of a single variety of starch or cellulose; and it is not unnatural, as Cross and Bevan hold, that a particular kind may often represent a mixture of different individuals. Moreover, the study of the subject is divided amongst agriculturists, physiologists and chemists, who christen the substances according to their special convenience or convention. In chemistry and chemical industry starch is named after the source from which it is produced; for example, rice starch, barley starch and potato starch are those made from rice, barley and potato respectively. As regards cellulose it may also be called after its source,

e. g. cotton, jute or flax celluloses which differ from each other slightly in chemical composition. In the plant tissues cellulose occurs in combination with other substances and also sometimes in the free state ; it is accordingly classified as compound-cellulose and free cellulose ; and further the former is termed according to the character of the substance combined with it which may be separated from cellulose-proper by some such process as hydrolysis ;* *e. g.* ligno-cellulose which gives lignin or lignic acid and cellulose, pecto-cellulose which yields pectic acid and cellulose, and adipo-cellulose decomposes into adipic acid and cellulose. Besides there is animal cellulose of which glycogen is a familiar example ; this, although of physiological importance, is not of any use from industrial aspect. For our present purposes *it would be convenient to call to the mind of the reader cotton in the place of cellulose, and rice or barley as the representative of starch,* because the chemical nomenclature may produce a little confusion.

* Hydrolysis may be roughly defined as a process of chemical change or decomposition which takes place with the addition of the elements of water ; the most familiar case of hydrolysis is the decomposition of cane-sugar into grape-sugar and fruit-sugar. For recent discussion of the theory of hydrolysis refer to Werner,—New Ideas on Inorganic Chemistry (1912), 215—219.

CHAPTER II.

General Chemical Character and Laboratory Syntheses : Synthetic Views of Structure.

Before proceeding to the interesting history of manifold industrial applications of starch and cellulose, it would be convenient to briefly consider the chemical character of starch and cellulose ; and for this rather unpalatable discussion of the subject, it is necessary to indulge in the patience of the reader.

6. General chemical character of the substances : hexoses their probable units of composition.—Starch and cellulose, as has been referred to before, are essentially substances of vegetable origin, and are chemically classed under the general name of poly-saccharose, so that cotton or rice consists mainly of substances belonging to the sugar-group ; but as the reader is well aware, each of them is far from tasting sweet ; and it is not possible to eat cotton or jute-fibres or barley-powder in

the place of sweet sugar. The relationship is a purely chemical one. The point is that when starch or cellulose is warmed with dilute hydrochloric or sulphuric acid the substance is, in a short time, disintegrated and almost quantitatively converted into the sugar glucose (grape-sugar) and dextrin; the quantity of sugar so produced can be identified and estimated by means of Fehling's solution * of known strength; and by knowing the amount of sugar produced from a definite weight of starch or cellulose, the quantities of this substance can be roughly estimated. It is thus found from the breaking up of the starch or cellulose molecule into end products—sugars (hexoses)—that, generally speaking, sugars of the grape-sugar type are the units of which the higher complex substances like starch and cellulose may be said to be composed.

It is well known that the sweet sugars, starch and cellulose are all chemically composed of

* A standard Fehling's solution may thus be prepared: A solution of 34.64 grams of carefully weighed copper sulphate in 500 c.c. of distilled water is made; then a second solution of 60 grams of caustic soda and 173 grams of Rochelle salt is prepared also in 500 c.c. of water, equal volumes of these solutions when mixed being known as Fehling's solution. The strength of such a solution is 10 c.c. = 0·05 gram of glucose.

only three elementary substances, namely carbon which is solid and most familiar to all in the form of black charcoal, and two other invisible, colourless and inodorous gases,—hydrogen and oxygen. The molecular formula for grape-sugar in solution has been found to be

Carbon (C)	Hydrogen (H)	Oxygen (O)
6	12	6

or to put it in plain symbols, $C_6H_{12}O_6$, which is evidently nothing but the hexa-multiple of CH_2O.

7. Synthesis of formaldehyde (monose) from the elements: Its conversion into formose (a hexose).—It is no small triumph of synthetic chemistry that starting with the elementary substances—black carbon and gas hydrogen—the substance of the simple formula CH_2O has been prepared, which is so well known to organic chemists by the name formaldehyde. * This formaldehyde, though gaseous at the tem-

* The recent researches of Bone and his co-workers [Bone and Jerdan, Trans., 41 (1897); Bone and Coward, 1197 (1908), 1975 (1910)] have shown that by heating purified carbon in an atmosphere of pure and dry hydrogen, under proper conditions, as much as 95% of methane can be prepared. From this synthetic methane, by the regulated action of chlorine, methyl chloride,—and from methyl chloride, by hydrolysis, methyl alcohol may be obtained; and then, by partial oxidation of the alcohol, formaldehyde is synthetically produced.

perature of the tropical Indian climate, is sold in solution under the name formaline,—an article of great industrial importance. It has a taste far from anything good and a sharp odour. Perhaps it is even a greater wonder that from this synthetic formaldehyde in the presence of magnesia or lime, under proper conditions, the chemist has succeeded in preparing a substance which has the same formula as that of natural grape-sugar and is as sweet as glucose itself. Prof. Loew's researches in this connection have greatly advanced our knowledge on the subject and deserve special mention.

8. Brief history of early attempts to synthesise Sugars.—The history of sugar-synthesis dates from Buterlow's observation in the year 1861; * but a substantial advance was made by Loew,† who observed that formaldehyde and lime-water yield a sweet syrup having the formula $C_6H_{12}O_6$ and satisfying the ordinary reactions of a hexose. This substance he named formose. The discovery has special importance, since it gave considerable experimental support, as will be found later on, to a theory advanced by Baeyer that carbon dioxide,

* Buterlow, Annalen, 120, 295; Compt. rend., 53, 145.

† J. prakt. Chem., 1886, 33, 321; Ber., 1889, 22, 475.

in being assimilated by the plants, passes through an intermediate stage of formaldehyde. Shortly after Loew's first observation, he modified his original method, replacing lime by magnesia * ; this time also he succeeded in obtaining a syrup which was found to possess almost all the properties of natural sugar including fermentability ; the new sugar was called methose. The subsequent investigations of Emil Fischer and his collaborators, who have been immortalised by their brilliant epoch-making researches in the sugar-series, have shown that Loew's formose and methose are complex mixtures containing A-acrose. They have succeeded in synthesising and isolating the hexoses as well as other lower and higher sugars.**

9. Constructive views of the composition of complex carbohydrates †.— The next higher substance in the carbohydrate-

* Ber., *loc. cit.*

** Lachman, The Spirit of Organic Chemistry, 114-153; and Ann. Rep. Chem. Soc., 1911.

† The formula of grape-sugar which is usually written $C_6H_{12}O$ may be expressed as $C_6(H_2O)_6$ in terms of carbon and water. It has been found that the majority of sugars, starch and cellulose contain hydrogen and oxygen in their proportion in water ; so that the composition of those substances may be represented by the general formula $C_x(H_2O)_y$; and this fact has given rise to the name hydrate of carbon or carbo-hydrate.

series is cane-sugar which is synthesised in Nature's Laboratory in immense quantities and with which people are so familiar. Cane-sugar is represented by the formula :—

$$\text{Carbon}_{12}\ (C)\ \text{Hydrogen}_{22}\ (H)\ \text{Oxygen}_{11}\ (O)$$

or to put symbolically, $C_{12}\ H_{22}\ O_{11}$. If dilute solution of hydrochloric or sulphuric acid is added to to cane-sugar solution and the mixture warmed, two sugars—grape-sugar and fruit-sugar —are produced in theoretically possible quantities ; and this conversion of two sugars of known constitution from cane-sugar by adding water may be plainly represented as follows :—

$$\underset{\text{(cane-sugar)}}{C_{12}\ H_{22}\ O_{11}} + \underset{\text{(water)}}{H_2O} = \underset{\text{(grape-sugar)}}{C_6H_{12}O_6} + \underset{\text{(fruit-sugar).}}{C_6H_{12}O_6}$$

At the present day, it is an established fact that, starting with the simplest inorganic elements, carbon and hydrogen, the simple organic substance formaldehyde can be prepared. We have now reached a position when we can pronounce that we are able to synthetically build up the complex structure of a substance closely allied to grape-sugar, starting from the elements carbon and hydrogen ; and we may put the stages in this series of syntheses roughly as follows :—

Carbon + Hydrogen* → Formaldehyde* → Formose
CH_2O $C_6H_{12}O_6$
akin to grape-sugar.

Then from two molecules of grape-sugar which is a compound of known composition and has been synthetically produced, isomaltose, a sugar isomeric with cane-sugar, has been obtained by the action of concentrated hydrochloric acid, the process being called *auto-condensation* :—

$$\text{Grape-sugar} \rightarrow \text{Cane-sugar}$$
$$2(C_6H_{22}O_6) - H_2O \qquad (C_{12}H_{22}O_{11}).$$

In the carbohydrate family starch and cellulose have still more complex structures ; and the synthetic chemist has not yet been able to prepare substances of like composition in Laboratoy.

10. Significance of the experimental results in explaining the synthesis in plant-physiology : Possibitity of cane-sugar-making from starch.—The above synthetic results are of remarkable significance in explaining the mysterious work in plant-physiology ; they reveal somewhat the hidden processes of Nature in plant-syntheses, as will

* Vide foot-note under paragraph 7.

be presently seen ; and although the results are only of theoretical importance at present, the knowledge of this may help great industrial achievements in days to come. We may look forward to a time when the manufacture of cane-sugar from starch by the application of electrical or some other form of energy may attain considerable industrial importance. Aubert and Giraud have already struck a note in this direction.* They state that by passing an electric current through acidified starch-paste at 100° C. cane-sugar may be manufactured. The rationale of the process, however, is not clearly understood ; but the assertion of Aubert and Giraud, which has been certified by subsequent investigators, may be received without any qualification. Convincing experimental evidence has now been obtained that the action of cold strong hydrochloric acid on starch results in rapid degradation, through usual successive stages, to maltose ; the speed of this change is much superior to that of the conversion of maltose into glucose.† It is interesting to note that the hydrolysis of starch by acids is similar to the decomposition of starch by the action of

* Ding. Pol. Jour., 257, 298.

† Daish, Trans., 105, 2053—2065 (1914).

the enzyme taka-diastase in which the successive formation of maltoses and glucose is clearly indicated by graphic methods.*

11. Molecular composition of starch and cellulose.—As stated before nothing definite has as yet been achieved about the molecular composition and structure of starch and cellulose. Cross and Bevan, the principal workers on cellulose, have greatly advanced our knowledge on the subject by their extensive series of patient researches ; this is, however, no place to enter into the complex details of their work. The simplest or empirical formula for starch and cellulose have been determined by quantitative combustion-analysis ; that is, by burning a known weight of starch or cellulose in oxygen gas and weighing the amount of carbon dioxide and water produced, and therefrom calculating the weight of carbon and hydrogen. From the weight of carbon and hydrogen so obtained, their percentage weight is found and empirical formula calculated. Starch and cellulose can not be gasified undecomposed, nor have any suitable solvents for them been obtained ; their molecular formulæ, therefore, have not been determined. They may be represented by

* Davis, Jour. Soc. Dyers, 30, 249, (1914).

$$(C_6 H_{10} O_5)_n$$

where n may be 4, 5 or any other number not known. Starch, however, is found to have the molecular weight about 645, corresponding with the formula

$$(C_6 H_{10} O_5)_4$$

in formamide solution ; * while Morris and Brown propose a wonderfully big formula for starch containing forty two hundred atoms, $C_{1200} H_{2000} O_{1000}$, all linked within a molecule ! Cellulose perhaps has a still heavier molecule !

12. Constitutional studies and general views on cellulose.—It is evident from what has been said that the exact mechanism of the resolution of cellulose into better known carbohydrates is not fully understood ; but the *gradual* resolution of it by means of sulphuric acid, through a series of compounds terminating with glucose or dextrin †, indicates a certain

* Walden, Bull. Acad. Sci., St. Petersburg, 1055-1082 (1911).

† The molecular composition of dextrin which is a yellowish powder, was hitherto not definitely known ; it was expressed by the formula $(C_6H_{10}O_5)_n$. Quite recently, Pringsheim and Eissler, who have been studying the Chemistry of Starch, have obtained as many as six crystalline dextrins from rice-starch as well as from potato. When rice-starch is fermented with *Bacillus macerans* part of the starch separates being unattacked by the organism. The solution is filtered ; and on adding chloroform to the filtrate,

constitutional relationship to the simpler carbohydrates. As the exact nature of the change is not known, it is impossible to draw any but general inference from the products of resolution ; and the safest conclusion is that, starch or cellulose molecule is a complex of molecules resembling the simpler and better known carbohydrates. Cellulose contains ten hydroxyl (-OH) groups, as it forms deca-acetyl derivative ; it is also conjectured that the bond which unites these carbohydrate-units is one of dehydration.* The recent researches of Loew upon the condensation of formaldehyde † lend some support to the probability of this view. The conversion of cellulose into aldehydic sugars clearly indicate the presence of aldehyde group (-CHO) in the cellulose-molecule. In view of the present knowledge of the subject, it is only possible to regard the cellulose-molecule as a complex of carbohydrate-units, containing alcoholic hydroxyl (–OH) and aldehydic oxygen (—CHO), the linking of

a crystalline deposit is obtained from which two varieties of dextrin-*a*, $(C_6H_{10}O_5)_4$, called tetra-amylose, and dextrin-*b*, $(C_6H_{10}O_5)_6$, named hexa-amylose, have been separated. Abs. Chem. Soc. i, 832 (1912) ; i, 1156 (1913). Ber., 47, 2565-2572 (1914).

* Baeyer, Ber., 3, 63 for a fuller account of the subject.

† Ber. 20, 141.

the sugar-units being perhaps effected through these oxygen atoms.*

13. Composition of cotton, linen and jute fibres.—Attempts have been made to get an insight into the nature of composition of the vegetable fibres. Pure cotton and linen consist essentially of cellulose and exhibit, in general, the properties of that substance on treatment with solutions of strong acids and other reagents. Jute, although resembling cotton and linen in its behaviour towards acids, differs from those fibres in chemical composition. Cross and Bevan, who have made a special study of the subject, have given the name bastose to the substance of which jute is chemically composed; this bastose, on being treated with solutions of caustic alkalis, yields cellulose and other substances related to the tannins. †

14. Chemical composition of wool and silk fibres: Difference between

---

* Bownam, Br. Asso. Rep., 1887.

† Cross and Bevan, Researches on Cellulose:

The views of Cross and Bevan (*loc. cit.*) may thus be put in short:—The substance, called bastose, of which jute is composed, is a ligno-cellulose and may be regarded as a complex molecule made up of three components or units, viz., ordinary cellulose, secondly, a penta-acetyl cellulose which contains an aldehyde group and yields furfurol on hydrolysis and lastly, a compound of the nature of a quinone which, on chlorination and reduction, yields derivatives of trihydric phenols.

animal and vegetable fibres.—The animal fibres, wool and silk, differ very materially from the vegetable fibres both in physical structure and chemical composition ; and it is on this difference in the chemical character of the fibres that their affinity for colouring matters and their dyeing methods depend. Vegetable fibres, as already referred to, belong to carbohydrates ; while the animal fibres come under a group of organic compounds, known as amino-acids. There is again difference between the composition of wool and silk ; wool contains sulphur, while silk does not. The name keratin has been given to the substance, of which wool is composed ; keratin has the chemical nature of a protein and is therefore amphoteric* in its reactions. Chemically speaking, silk is also a protein. It is found to be composed of two substances, called sericin and fibroin.

* A compound, of which the constitution is such that, it is capable of behaving either as an acid or a base, is called an amphoteric substance. The simplest organic compound of amphoteric nature is glycine or amino-acetic acid ; by virtue of its acidic carboxyl-group, it reacts with alkalis and forms salts, while owing to the presence of basic amino-group, glycine also forms salts with strong acids. Some metallic hydroxides, for example, those of aluminium, zinc, etc. are also amphoteric in character. For fuller information, *vide* Werner,—New Ideas on Inorganic Chemistry, 214.

CHAPTER III.

Synthesis in the Plant-System.

15. Occurrence of starch and cellulose in the plant-system.—We are now proceeding to an interesting phase of the subject, namely, the occurrence and formation of starch and cellulose in the plant-system. We have seen the amount of success in synthesis attained in man's Laboratory, wherein the chemist has achieved interesting results up to cane-sugar. The knowledge of the structure of a compound generally precedes its synthesis ; and attempts to go higher and to build more complex carbohydrates have not been crowned with success, as their constitution is not known. We have now to consider syntheses of starch and cellulose in Nature's Laboratory. We know her success is immense ; this is clearly proved by the fact that she produces vast quantities of these materials ; and we are only to try to take away from her the secrets of her processes.

Cellulose forms the essential ingredient of the cell-walls of all plants and is found to have, when examined under the microscope, an

organised structure ; while starch is present in almost all parts of the plants, but it is specially stored up in the seeds, the pith of stems, the bulbs and roots. Generally speaking, starch is found in those parts of the plant-system which serve as a store for reserved material for the future nourishment of the plants.

16. Secrets of Nature's process: Her simple Laboratory.—To-day a seed is sown and in some years it will grow to a mighty tree, the plant continuously synthesising in itself starch and cellulose for its nourishment and body-building. The questions naturally arise—where does the plant get its materials for preparing these substances in its system and what is the mechanism of its synthetic processes ? It must be said that Nature has neither the flask, the test-tube, the gas-burner and the electric furnaces nor the peculiar condensing agents and the high-priced pure chemicals which the chemist uses in his experiments ! For the plant, the materials to start with are very simple : —carbonic acid gas and moisture of the atmosphere in which the plant is enveloped, its magic reagent—chlorophyll—which is the green colouring matter of plant-leaves, and, instead of a gasflame or electrical energy, the vast store of

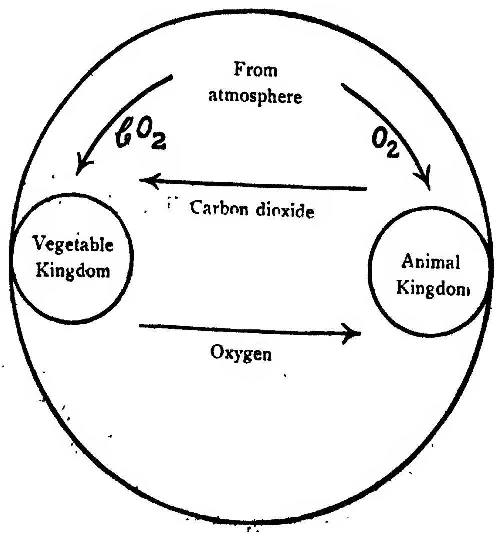
sunlight which shines on the plant from morning to evening. How beautiful, how simple, how divinely equipped is Nature's Laboratory! Carbon dioxide, moisture, chlorophyll and sunlight are all that is necessary to build up the complex substances; perhaps a fourth factor, namely, the mysterious intervention of protoplasmic action of plant-cells, is present. The mechanism in plant-syntheses, however, is not fully understood. It appears that chlorophyll enters into these processes in some way, perhaps as a "contact" substance.

A new idea has, however, been suggested by Wager,* who has made a study of the action of light on chlorophyll. He suggests that the production of sugars, starch and other carbohydrates in the green leaf may be initiated by the photo-oxidation of chlorophyll and subsequent condensation of the aldehyde, produced from the decomposition (of oxidised chlorophyll), rather than by the direct photo-synthesis of carbon dioxide and water.

17. Mutual compensating benefits between animal and vegetable kingdoms: the carbon-cycle.—The carbon dioxide of atmosphere is reduced by the joint

* Wager, Proc. Roy. Soc., 87, 386 (1914).

action of chlorophyll and sunlight, the carbon being assimilated by the plant for its body-building and nourishment, oxygen which is necessary for animal-life, being partly set free. This process of assimilation does not take place during night when sunlight is absent. The process is thus one of many instances of complementary and compensating benefits between the vegetable and the animal kingdoms, bearing on their mutual life and growth. The above Carbon-Cycle may be graphically represented as given below :—



The oxygen, given up by plants, is necessary for the life of animals, whilst the carbon dioxide, exhaled by animals, is taken up by the plant for its life and growth, as shown by the arrows.

18. Probable steps in the synthesis of starch and cellulose in Plant-system.—It was supposed that the influence of sunlight in effecting synthesis in plants is greater in the tropics than in temperate countries ; but recent investigations have shown that this is not the case ; it has been found that, when the sky is clear, photo-synthesis proceeds with the same rapidity everywhere ; and the lower results, obtained for countries in higher latitudes, are due to a higher percentage of dull days.

Attempts have been made to understand the synthetic processes in plants ; and researches are in progress in some laborataries under the name of photo-chemical syntheses * in plants.

* Many chemical changes are brought about by the influence of light (photo). Instances of oxidation, reduction, polymerisation and other synthetic reactions of this class are well-known. For further information, *vide* the article on "Polymerisation of unsaturated compounds and Photo-chemical changes", Ann. Rep. Chem. Soc., 1911.

A series of papers on Chemical Action of Light, Ciamician and Silber, Ber., 1911-13.

Photolysis of sugars, etc., Gaudechon, (1912), 155, 1506-1509.

Photolysis of ethyl alcohol, etc., Berthelot and Gaudechon, Compt. rend., (1913), 156, 68-71.

The reactions involved in the process are not, as has been said before, fully understood. The formation of starch from carbon dioxide and moisture under the influence of chlorophyll and sunlight may be symbolically respresented thus :—

$$\underset{\text{carbon dioxide}}{(6CO_2} + \underset{\text{moisture}}{5H_2O)_n} = \underset{\text{starch}}{(C_6H_{10}O_5)_n} + \underset{\text{oxygen set free}}{(6O_2)_n}$$

The solid complex starch is not, however, formed at once from carbon dioxide and moisture as represented; but is, in all probability, produced from glucose which precedes the formation of starch and cellulose; the production of starch or the more complex cellulose-molecule † may, then, be conveniently put on paper as follows :—

$$\underset{\text{glucose}}{xC_6H_{12}O_6} - \underset{\text{water}}{xH_2O} \rightarrow \underset{\text{starch or cellulose}}{(C_6H_{10}O_5)_x}$$

† The Cellulose-molecule is here shown to be formed from an aldo-hexose (glucose) which was, until recently, identified with the reducing sugars, obtained from degradation of cellulose. It has, however, been found that the various forms of cellulose contain the groups or nuclei identical with that contained in lævulose (fruit-sugar), that is, keto-hexoses or those substances which produce keto-hexoses by hydrolysis; such keto-hexoses or nuclei constitute the main or essential part of the cellulose-molecule, and not glucose as hitherto supposed. Fenton and Gostling, Trans., 79, 360 (1901).

It appears highly improbable again that substances of such complex structures as those of glucose, starch and cellulose would be formed in so simple a fashion from moisture and carbon dioxide. As in masonry huge edifices are built up in stages by carefully laying each piece of brick or stone which requires an amount of time and a degree of skill, in the organic world as well Nature displays an amount of skill in the construction of these highly complex molecules, the secrets of which have not yet been attained by the chemist. It is probable Nature also builds up the heavy structures in several stages. Various theories have been put forward as to the nature of the reaction between carbon dioxide and moisture at the initial stage; to some of these we shall turn in the next chapter.

The nature of condensation of the initial products has also been a subject for investigation. Gibbs and Freer * have studied the localisation and function of potassium in plants as a condensing agent. By means of Macallum's reagent † they have detected its presence in all parts of the plant-system, but found it absent in

* Gibbs and Freer, Jour. Phys. Chem., 16, 709 (1912).

† A mixture of sodium cobaltinitrite, ammonium sulphide and glycerine is known as Macallum's reagent.

the chlorophyll-regions. The view, as put forward by Grafe and Stocklasa, ‡ that the condensation of aldehydic or unsaturated products into higher carbohydrates may be effected under the influence of alkalis present in the plants, is supposed to be opposed to the above experimental work by Gibbs and Freer. It should be observed, however, that the absence of potassium in the chlorophyll-regions does not prove that the alkali in other parts of the plant-system cannot act as a condensing agent ; for, it is not absolutely necessary, according to the theory of Grafe and Stocklasa, that the complex carbohydrates should be formed only in the chlorophyll tracts. It is quite probable that, the initial products, as soon as they are formed, migrate to the alkaline regions where they undergo further processes of condensation or assimilation.

‡ Grafe and Stocklasa, Biod. Zentr., 41, 762 (1912).

CHAPTER IV.

Theories on the Mechanism in Plant-Synthesis.

19. Oxy-methylene theory of synthesis in Plants.—Numerous attempts have been made to explain the mysterious processes of Nature. A new view * in the light of recent work on the subject, as advanced by Sernagiotto, holds that, initially, reduction of carbon dioxide and simultaneous combination between the reduced gas and moisture take place with the elimination of oxygen and production of what is called oxy-methylene. Oxy-methylene has the simple formula $=CH.OH$ and is isomeric with formaldehyde which, as seen before, has the formula $H.CHO$. The formation of oxy-methylene may be represented thus :—

$$CO_2 + H_2O \rightarrow \underset{\text{oxy-methylene.}}{=CH.OH} + O_2$$

The unsaturated oxy-methylene, so produced under the influence of chlorophyll and sunlight, is unstable and incapable of isolation from

* Sernagiotto, Gaz. chim. ital., 44, i, 622—31 (1914).

its very nature of constitution. As soon as it is formed, it undergoes a change known as *polymerisation*, during which process more complex substances of multiple formulæ are produced; oxy-methylene, according to this hypothesis, polymerises into a compound of the type of inositol, $C_6H_6(OH)_6$, which is widely distributed in nature; and this inositol may give rise to glucose or fructose by some such process as tautomeric rearrangement or hydrolysis.

The scheme may be plainly put as follows:—

$$\underset{\text{oxy-methylene}}{6{=}CH.OH} \quad \underset{\substack{\text{viâ} \\ \text{inositol-type}}}{\longrightarrow} \quad \underset{\text{glucose or fructose}}{C_6H_{12}O_6}$$

and similarly it may be applied to explain the formation of other higher or lower molecules. Although oxy-methylene, owing to its unsaturated character, has the advantage of belonging to the group of substances which readily undergoes photo-chemical changes, the *oxy-methylene theory* does not seem to have been favourably received in the chemical world, as sufficient experimental evidence has not been forthcoming in favour of the view.

20. Formaldehyde theory in Plant-synthesis.—The more generally accepted view, however, is the *formaldehyde theory*, because the

chemist has succeeded in synthesising sugars from it, to which reference has already been made.* A solution of formaldehyde under the influence of baryta water or magnesia is converted into formose, methose or acrose, as differently christened ; each of these, in formula and chemical properties, bears close relationship to glucose or fructose. Although evidence is slender, the chemist seems to be often inclined to explain the natural processes *exactly* after the fashion of his laboratory-experiences. Baeyer † first advanced the formaldehyde theory of syntheses in plants ; and it has been supported, to some extent, by the experimental evidences of Loew. According to this theory, formaldelyde which is initially produced from atmospheric carbon dioxide and moisture, undergoes polymerisation to successively form sugar and starch mainly in the plant-leaves, the changes being effected by the joint influence of chlorophyll and sunlight.

21. Further evidences in favour of the theory.—Various suggestions have been made to explain as to how the process, in its primary stages, is actually initiated. Additional

* Vide pp. 11-14 of this book.

† Ber., 3, 67.

strength to the formaldehyde theory comes from recent researches. Formaldehyde has been produced from carbon dioxide and moisture; and sugars have also been obtained by the condensation of this aldehyde. In attempting to prepare formaldehyde from carbon dioxide and moisture by means of electric discharge, a mixture of glycolaldehyde and formaldehyde has been obtained which may be roughly shown as follows :—

$$\underset{\text{(Carbon dioxide)}}{CO_2} + \underset{\text{(moisture)}}{H_2O} \rightarrow \underset{\text{(glycolaldehyde)}}{\begin{array}{c} CH_2OH \\ | \\ CHO \end{array}} + \underset{\text{(formaldehyde)}}{H.CHO}$$

If carbon dioxide is replaced by carbon monoxide in the experiment, a better yield of formaldehyde is obtained, as represented :—

$$\underset{\text{(carbon monoxide)}}{2\,CO} + \underset{\text{(moisture)}}{2H_2O} \rightarrow \underset{\text{(formaldehyde)}}{2\,H.CHO} + \underset{\text{(oxygen)}}{O_2}$$

It is therefore concluded that carbon dioxide is perhaps, in the first stage, reduced to carbon monoxide which goes to form formaldehyde.

Quite recently, formaldehyde is stated to have been detected in the plant-leaves in minute traces; this would evidently lend great support to the view.

22. Glycolaldehyde theory of Synthesis in Plants.—Fincke,* who has studied the formation of carbohydrates in plants, is of opinion that during assimilation the reduction of carbon dioxide of the atmosphere is accompanied by the formation of a chain of two interlinked carbon atoms, glycolaldehyde being the chief intermediate product; and from this, sugars as well as other vegetable products are said to be formed by condensation. The assumption that glycolaldehyde is the intermediate product in the synthesis of carbohydrates is, however, in better agreement with experimental facts, referred to in the preceding paragraph, than the formaldelyde theory. But it is difficult to accept the *glycolaldehyde theory*; because it is almost impossible to suppose, as Fincke does, the formation of oxalic acid from carbon dioxide at once which then gives rise to glycolaldehyde; and moreover, the theory can not easily explain the formation of compounds containing an odd number of carbon atoms.

23. Important role played by Osmosis and Mass Action in the life and growth of plants.—As soon as the carbo-

* Fincke, Abs. Chem. Soc., i, 466 (1914); Biochem. Zeit., 61, 157 (1914).

hydrates are produced in the plant-leaves and other green parts of plants, they are transported in solution or partly in liquid-crystalline condition * (?) through the veins and arteries of the plant to other parts of the plant-system where they are utilised in building up its tissues (cellulosic matter) or stored up as a reserved material, mainly as starch, for its future nourishment. It is well-known that watery substance and food, necessary for plant-life, are taken up by the plant from moist soil which contains them; † the lower parts of its system are therefore more sappy, while its upper parts are richer in carbohydrates at any particular time of their production. The concentration of the carbohydrates in solution thus being greater in the green or upper parts of the plant, these substances continually pass to the regions of lower concentration by virtue of the laws of osmotic pressure. It is evident that the carbohydrates cannot be localised in the zone of their production; for as long as the plant is healthy and can take up liquid matter and food from the

* Under the influence of a stimulant, a local or transitory anisotropic form may be produced. Lehmann, Biochem-Zeit., 63, 74, (1914).

† Knop, Versuchs-Stationen, vii, 252.

soil,* a difference in concentration between the higher and lower parts of the plant is maintained, and consequently, the above process of transport is continuous. The greater the speed of migration of the carbohydrates,—the reaction-products—at a particular moment, the greater also would be the velocity of their synthesis, owing to the carbohydrates being transferred from the field of production. It is thus quite interesting to observe that the phenomena of osmosis and the laws of mass action play important rôle in the life and growth of plants. The history of plant-syntheses from carbon dioxide and moisture also makes it clear that, in the organic world, matter passes from a simpler to a more complex state.

24 Nature *versus* Chemist : a struggle for supremacy.—Though the development of synthetic chemistry has been marvellous in recent years, a summary judgement on Nature's processes by the Chemist (one of the parties concerned) is not likely to be equitable in a struggle of Nature *versus* Chemist. So Nature is perhaps justified in raising a discordant voice. She proclaims—"Well, Chemist, you say you

* Gris, Water Culture, 200 ; Boussingault, Compt. rend., 883 (1864).

can extract my chlorophyll in your laboratory; moisture and carbon dioxide with which, you say, I start on my work, you can get enough from the atmosphere or you can prepare them at will; the agency of sunlight which, you say, is necessary for me, you can use at pleasure. Well, then prepare me a quantity of sugar, starch or cellulose! Why do people cultivate, kill and press sugar-canes in the East Indies or colonise the distant Fijis for the purpose at the expense of so much cost and labour? Why do they plough the paddy or wheat-fields and thrash the corn with the sweat of their brow? Why are they so busy in cultivating jute, cotton and flax?" The chemist is here silent at present; and although such passionate queries of Nature may not be satisfied, he hopes to reveal the mysteries of her processes and explain them in time to come; there is thus no possibility of synthetic industries in these directions in near future.

25. Co-operation between Nature and the Chemist.—It may, however, be suggested that, instead of a spirit of challenge, there should be a permanent policy of *conciliation* and *co-operation* between Nature and the Chemist. It is a plain fact that Nature turns out vast quantities of raw materials; and it is the business of

the Chemist to convert them into commodities fit for human use. It is at the same time imperative that the Chemist should supply Nature with fresh energy, in order she may enormously increase the vegetable resources of a country—starch and cellulose amongst these. Here lies the common platform where the necessity for co-operation between scientific agriculture* and chemical industries, based on vegetable raw materials, is of supreme importance.

26. Action of Chlorophyll when present in living plants and when extracted : Explanation of its synthetic action from parallel instances and in the light of Dr. Bose's researches.—It is possible that Nature possesses some artifices—

* In India, agriculture depends on the natural fertility of the soil, proper flood and rain. Scientific agriculture which examines the soil, diagonises its defects and prescribes requisite manuring, controls proper irrigation and chooses the best seed, is confined to a few costly experimental farms. It is necessary to popularise the cheap and successful methods of these experimental stations at the cost of the Government, the Ruling Chiefs and the Rájás in the beginning ; and once the illiterate cultivators are initiated and realise the excellence of the methods from example and experience, they will, of their own accord, come forward and adopt them. By a judicious application of scientific agriculture, the vegetable resources of India can be enormously increased. Compare Bulletins of the Department of Agriculture, U. S. A.

life-processes—which play an easy and important rôle in *the fixation of carbon* in the plant-system, perhaps through the protoplasmic action of *living* plant-cells. The point is that, as in Inorganic Chemistry, some substances which act as energetic *contact* substances, are poisoned or rendered *passive* or inactive under certain conditions, owing to some change in their atomic rearrangement or some other cause, it may be possible that parallel phenomena may happen as well in the Organic world with regard to chlorophyll which also acts as a mysterious *contact* agent. Chlorophyll may be called the plant-hæmoglobin,—a substance of extremely complicated structure, exactly similar, as has been recently found, to that of hæmoglobin of our blood ; there is chiefly only this interesting difference that there is magnesium in chlorophyll, whilst in hæmoglobin there is iron, each metal forming a complex ion or group with other elements or radicals in the respective compounds. Chlorophyll acts as a carbon-carrier, while hæmoglobin that of oxygen. It is quite interesting to note that this chlorophyll may be rendered *passive* or inactive, as in the case of an Inorganic contact substance, owing to some change in its constitution which takes place during the

process of extracting it with a reagent; or it may not be improbable that it may be *poisoned*, that is, rendered unconscious or paralysed under the influence of the extracting agent; and therefore it becomes devoid of its synthesising rôle which it plays in the *living* plant-system.*

Before concluding the fascinating subject of the **fixation of carbon** by plants, it is necessary to point out that the volume of carbon dioxide is only $\frac{3}{10,000}$ of the atmosphere; but the volume of the latter is sò tremendously immense that, when taken in its entire weight, it contains no less than 3,400,000,000,000 tons of carbon dioxide! This amounts to about 28 tons over every acre of the surface of the earth.

---

* This view is put forward in the light of the latest researches of Dr. J. C. Bose of Calcutta. The bearing on the subject may be put in short thus:—In throbbing or living organisms, animal and vegetable, the rhythmic pulsations come to a stop at the moment of death. The difference between the conditions of a tissue, living and dead, is one of molecular transformation from a state of mobility to a state of interlocked rigidity. At the crucial moment, particles of the living tissue are swinging in their unstable poise; a little tilt one way and the molecular mechanism becomes interlocked in death. Sleep is a phenomenon which mimics death. (Dr. Bose on "Death-Spasm in Plants" at the Calcutta University Institute, 1914.) It seems not improbable that chlorophyll, *when abstracted* from the living plants, represents a condition of paralysis or death and therefore does not possess the synthetic power it plays *when present in the living* vegetable organs.

CHEMICAL INDUSTRY

OF

Starch and Cellulose

CHAPTER V.

Some Thoughts on Industrial Problem in India.

27. Industrial training and education in India.—It is often said that the people of India lack in industrial and commercial training and do not develop what is called "business-knack." Generally speaking, they strive for University degrees, join the bar or enter some walks of life other than commercial ; and for this can they be made totally responsible ? One aspect of the problem, however, may be briefly put here. The system of University Education* which works up

---

* Brown, University Training of Technical Chemists, Jour. Soc. Chem. Ind., 28, 279 (1909).

Burgess, The Efficiency of College Training of Men for the Chemical Industries, Jour. Amer. Chem. Soc., 33, 611, (1911).

Dennis, To what Extent should College Training confer Practical Training along Technical lines ? Jour. Ind. and Engin. Chem., 1, 194 (1909).

James, Chemical Education for the Industries, Proc. of Soc. for the Promotion of Engin. Educ., 19 (1912).

Kaempffert, The Industrial need of Technically trained men : Scientific Manufacturing and the Opportunities it offers, Sci. Amer., March, 15 (1913).

the manhood of a nation is considered to be defective from this point of view. Technical education has little place in its curricula ; and there is, strictly speaking, no technological institution of importance affiliated to any University in India. It also appears advisable that scientific men and economists, having special industrial studies and researches, should be appointed to work in technological institutes*

Lunge, Education of Industrial Chemists, Jour. Amer. Chem. Soc., 15, 481 (1893).

Nichols, The Efficiency and Deficiencies of the College-trained Chemist when tested in the Technical Field, Jour. Ind. and Engin. Chem., 1, 102 (1909).

Pemberton, The Education of Industrial Chemists, Jour. Amer. Chem. Soc., 15, 627 (1893).

Stewart, A Plan for the support of Chemical Research and for the better Teaching of Industrial Chemistry, Jour. Ind. and Engin. Chem., 4, 616 (1912).

Withrow, Points of view in the Teaching of Industrial Chemistry, Jour. Amer. Chem. Soc., 33, 624 (1911).

Symposium on the Education of the Technical Chemist, Chem. Eng., pp. 71, 131, 210, 305, 357 (1904 – 5).

* These technological institutes should contain all necessary sections for practical instruction to students, including even commercial correspondence and the science of advertising. But it is of foremost importance that each branch of science in which instruction is to be given must have a small factory wherein the students, under the able guidance of an expert, must acquire first hand experience in the manufacture of articles from alpha to omega ; and the products of the institute-factories should be advertised and sold in the market. Compare Bacon, The Object and Work of the Mellon Institute, Jour. Ind. & Engin. Chem., April, 343 (1915).

Maclaurin, Talbot and Walker, The Universities and Industries, *ibid*, Jan.,. 59-64 (1916). Little, The University and Business, *loc. cit.*

or factories for a particular term of years; and after the expiry of this period, those who have academic distinctions in addition, may be transferred to the Colleges for teaching science and economics. After a certain number of years again the teachers of science and economics should be shunted to factories or State technological institutes affiliated to a University.

28. Advantages of the teacher-expert-shunting system.—This system has elsewhere met with considerable amount of success. It has manifestly manifold advantages, of which the following may be noted :—

First, as the maxim goes—the bow must not be always bent, and a break in the monotony of life and work of teachers is necessary. An exchange between academic and industrial services would serve to sharpen the activities of persons on either side and add fresh energy for work.

Secondly, a co-operation like this between the allied spheres of work will serve to grow up a healthy and progressive system of industrial organisation, aided by the judicious application of up-to-date culture and researches of the scientific or economic experts.

Thirdly, when in academic chairs, the experts, as teachers, will, in course of their class-lectures and conversation, incidentally impart to the students a general commercial information, and thereby serve to create and keep up the *industrial mind* of a nation.

Fourthly, such a system of teacher-expert-shunting is considered to prevent the accumulation of *mental rust* such as would seize on the teachers or experts during their purely uninterrupted and monotonous duties of 25 or 30 years in either capacity, in as much as the shunting method would help them to keep abreast of recent developments of the different phases of science—theoretical and applied.

Lastly, it will conduce to the many-sided intellectual and material advancement of a country.*

We now drop this topic, an elaborate discussion of which is not within the space at our command and return to the main theme of our subject,—the *application of starch and cellulose* in modern industries.

* Compare Hesse, Contributions of the Cheimst to the Industrial Development of the United States : A Record of Achievement, Jour. Ind. & Engin. Chem., April, 293 (1915).

CHAPTER VI.

Manufacture of Starch and its Miscellaneous Industrial Applications.

Starch and cellulose are the parents of numerous industries, mere brief description of which would go to make volumes. It is, however, not within the purpose of the present work. The vast fermentation industries for the manufacture of alcohols, the gigantic textile organisations for making cellulosic fabrics and the extensive application of cotton in the manufacture of dangerous explosives are outside the space at our command and will be only summarily noticed, as exhaustive treatments on them will be found in special works on the subjects.

29. General principles of Starch-manufacture.—The general principles for the manufacture of starch consist of the following successive stages of operations :—

First, crushing potato, wheat, rice or maize and triturating the crushed substance with a dilute solution of caustic alkali :

Secondly, washing starch-granules from the pulp produced in the first stage :

And thirdly, purifying and drying the starch.

The starchy material from which starch is to be prepared is placed in a grinding cylinder made of wood with iron-plate rollers, fixed half-way in water in order to cleanse the pulverised starchy pulp. Recently however, grinding cylinders with saw-teeth have come into use ; the saw-blades in these machines lacerate the starch-cells in a short time and in an efficient manner in order to obtain the starch-granules. A cylindrical metal-sieve is generally employed for separating starch-granules from the pulp. The granules are suspended in water, thoroughly washed and allowed to settle to the bottom of a trough. The granules are then crushed between steel-rollers to separate the starch from the fibre. They are then further washed and cleansed. The water is strained off by means of a centrifugal machine ; the fresh starch is now dried in rooms at about 60°C., and again crushed between iron-rollers. Of late, the centrifugal machine has also been introduced for drying starch.

30. Constituents of some varieties of commercial Starch.—Some varieties of

commercial starch are coloured blue or yellowish with ultramarines—a class of inorganic sulphur colours. According to Wolff, the constituents of commercial starch are as follows :—

	Finest pure potato-starch with bright crystalline appearence.	Finest blue patent-starch.	Pure wheat powder.
Water ...	17·83	15·38	14·52
Gum ...	——	——	0·10
Fibre ...	0·48	0·50	1·44
Ash ...	0·21	0·53	0·03
Starch ...	81·48	83·59	83·91
	100·0	100·0	100·0

31. Miscellaneous applications of starch,—in laundry, textile industry etc. : use in Bengal.—Starch is used for stiffening domestic articles in washing and also for setting up glossiness to stiffened textures ; it is largely used for sizing and stiffening papers and for finishing linen and cotton manufactures ; it is also employed in making arrow-root, gums, sago, syrups, vermicelli, dextrin and grape-sugar. For laundry purposes, potato-starch is generally preferred to other varieties ; but where great stiffness is requisite, wheat-starch is used, e.g. in book-binding. Potato-starch, however, being transparent is suitable for stiffening fine linen.

The Bengali washermen, as a rule, do not purchase the patent-starches for stiffening clothes, excepting seldom for glazing purposes. They follow a quite indegenous method. They overboil rice, preferably freshly husked rice from new paddy, with excess of water, and thoroughly stir it towards the end of the operation. The mixture, while hot, is strained through cloth and the syrupy extract so obtained is used by them. The process is easy and economical, whilst they are saved from purchasing patent rice-starch which is largely manufactured in England, France, Belgium, Germany and other countries for laundry purposes at a considerable cost and labour.

It is also interesting to note that the weavers in Bengal use their own preparations of starch in order to stiffen the handloom-made cotton textiles ; this process, though not so refined, is cheaper and less troublesome. In making *máree* or starchy extract, boiled rice is mixed with excess of water and kept overnight. It is then macerated, diluted with water and filtered through cloth. The course cotton fabric which is only stiffened by this method is hung and stretched on two hinges of bamboo-sticks at two ends in a shady place, preferably in the morning sun.

The *máree* is now sprinkled over the texture with a small hand-distributor and then evenly brushed with a large brush.

32. Manufacture of Arrow-root: origin of the name.—There are various kinds of arrow-roots—Indian, Brazilian, English etc. They are all made, at the present day, from starch which is obtained from different sources. The history of origin of the term arrow-root is interesting, and cassava-starch deserves special mention in this connection. The roots of manioc from which cassava—a kind of starch—is prepared and other analogous roots contain a poisonous juice; and arrow-root derives its name from the fact that the juice was used by the West Indians as a poison for the tips of their arrows.

33. Use of Starch for manufacturing tinned patent-stuffs and Biscuits.—Starch, in finely powdered form, for infants' food or patients' diet constitutes a large industry, *e.g.* tinned barley, corn-flour, *shatee* and other patented stuffs. It is used by confectioners to some extent, and in large quantities for the manufacture of different kinds of biscuits from the costly varieties to the cheapest ones. The difference in the quality of biscuits is chiefly due to the quality of starch, kneading, the uni-

formity of temperature at which they are baked and other ingredients employed by the manufacturers. It is a business-principle that often the manufacturers set different prices to the same quality of article under the name of different brands, as they are called ; and every one is aware that the higher priced stuff appeals to the customer to be a product of superior quality.

34. Starch for making various kinds of Gums.—Starch is employed to some extent in the manufacture of several patent gums, as familiar forms of which may be mentioned British gum, dextrin-gums, starch-gum and Alsace-gums. The dextrin-gum which is conveniently made from potato-starch is cheap and is largely used as a substitute for gum-arabic. The gums are chemically expressed by the empirical formula $C_6H_{10}O_5$ and are prepared by boiling starch with a small quantity of almost any *dilute* acid which thins its consistence and converts it into a soluble adhesive substance like gum-arabic.

35. Manufacture of Dextrin from Starch: its important uses.—The preparation of dextrin from starch by means of gentle heat is an easy operation. For this purpose starch is roasted in large iron drums until it becomes brownish yellow at 85°-110°C. The starch changes

into dextrin in an hour or so ; by adding water to dextrin, white dextrin-syrup or gum-syrup is obtained. It is also produced, as already stated, by treating starch with dilute acids. Quite recently, however, crystalline dextrins* have been obtained which are only of theoretical importance at the present moment. Dextrin is extensively used in printing wall-papers, in stiffening and glazing cards and paper, as a lip-glue, for surgical purposes and wines ; it has also a variety of applications in fine arts.

36. An interesting use of Tamarind-starch by Indian Kumáras.—The wheat-starch is generally used in making book-binder's gum which is obtained by boiling flour with water. An interesting use of starch in Bengal may be mentioned here. The idol-makers, the Hindu *málákaras* or *kumáras*, as they are called, skillfully extract a very fine form of starch from tamarind-seed by boiling the seed, crushed or uncrushed, with water in an earthen pot. In doll-painting when the preliminary operations are over, they paint the images with the starch-extract which acts as a size and sets up a gloss to the image when painted in colours. In times of

---

* Vide foot-note pp. 17-18.

severe famines, the seed is used as food by some aboriginal tribes.

37. Starch in the manufacture of Condensed Milk : an industrial abuse.—A common use of powdered starch is often made in the manufacture of condensed milk—skimmed or unskimmed. This use of starch as an adulterant in condensed milk, though not unscientific and so objectionable from dietatic point of view, is rather an industrial abuse. It is a fact that often a sticky starch-paste, whitened with a small quantity of milk and sweetened with as much as 40 per cent of sugar, passes for condensed milk. Condensed milk of various makes is largely consumed in India ; but educated Indians have not turned their attention to this industry which offers good prospects of success in Hindustan—the land of *dugdha* (milk) and *ghrita* (clarified butter). Some scientifically ill-informed people have thought that condensed milk is nothing but concentrated milk, the well-known Indian *kshira* or *málaï*, packed in tin-cans. The milk, so prepared and preserved, turns rancid in a short time and undergoes slow putrefaction. Although the industry has important bearing on the dairy-farm system, under normal circumstances also, there is a fair possi-

bility of success on a modest scale as the supply of milk in mofussil may be had from the *goalás* or milk-men, who make contracts for milk over a wide radius in the country. The Indian milks may compete favourably with the existing manufactures in quality and price ; and there is one important advantage that here, in India, there is a ready market for the commodity in this age of tea-taking and scarcity of pure milk in towns. Let us now turn to the subject with which we are directly concerned.

CHAPTER VII.

Starch and Important Chemical Industries.

38. Action of Acids on Starch: Manufacture of Soluble Starch.—Starch dissolves in *cold* concentrated nitric acid; and on adding water to this solution an explosive granular substance, known as xylodine or white gun-powder, is precipitated which is largely used in pyrotechniques. By *boiling* starch or sugar with strong nitric acid, oxalic acid is obtained as the final degradation-product with evolution of copious nitrous fumes. Dilute mineral acids or diastase convert starch into grape-sugar and dextrins which are crystallisable with difficulty. This process is employed in the manufacture of grape-sugar which is also prepared by decomposing cellulose and similar vegetable matter with dilute acids. Grape-sugar is largely consumed in wine-making and in the brewing of beer; it is used, to some extent, in confectionery and for colouring *liquers* or vinegars brown. Grape-sugar

occurs in many sweet fruits, as its name indicates, and forms the solid crystalline portion of honey.

It has been found that the best method of manufacturing the modification of starch, known as **soluble starch**, as well as dextrin consists, according to Browning and Barlow,* in passing hydrochloric acid gas or a spray of the aqueous acid into a rotary converter containing the starch. To produce soluble starch a temperature of 54°C is recommended, while for making dextrin the temperature should be maintained at 76°–93°C. The process by using gaseous hydrochloric acid is substantially confirmed by Frary and Dennis.†

39. Fermentation Industry: Numerous Industrial application of Alcohol.—But the most extensive application of starch in chemical technology is in the fermentation industries. With the exception of methyl alcohol which is obtained commercially as a bye-product from the destructive distillation of wood, the other important aliphatic alcohols are mainly produced by fermenting starch; and more recently, the higher alcohols have been obtained from crude cellulosic matter, *viz.* wood or saw-dust,

---

* Browning and Barlow, French Patent, 336, 903.

† Frary and Dennis, Jour. Soc. Chem. Ind., 7, March (1915). Compare also Allen, Commercial Organic Analysis, 3rd. Ed., 1,49.

by applying special methods of fermentation. Enormous quantities of alcohols are employed, directly or indirectly, in the chemical industries. Ethyl alcohol which is commonly known as alcohol is the most important member of the class ; it is the intoxicating principle of spirituous liquors.

Alcohol is largely used in chemistry as a solvent for determining molecular weights of compounds and in industry, for preparing pure substances by crystallisation. It is a good solvent for resins ; and for this property, it is largely employed in the manufacture of special kinds of varnishes and cements. The solvent property is also utilised in making some pharmaceutical preparations, *e.g.* tinctures or extracts. Absolute alcohol is used in preparing a homeopathic medicine of requisite dilutions. It has also the property of dissolving carbon dioxide which is used in the manufacture of effervescing wines, a well-known variety being champagne. Wines are sometimes coloured with caramel, a dark brown substance which is prepared by heating cane-sugar to 210°—220°C. In chemical industries alcohol is largely used for the manufacture of vinegar (acetic acid) by the action of certain chemical oxidising agents and oxidases. Large

quantities are also consumed for preparing ether, chloral, chloroform and various alkyl derivatives for employment in the coal-tar-dye industry. In museums a considerable quantity of alcohol is used for preserving anatomical specimens.

40. Manufacture of Artificial Perfumes and Scents.—In perfume industry alcohol is used for making various artificial fruit and flower essences which are often commercially known as "flavouring ethers." The higher alcohols are largely used in the preparation of the so-called fruit essences which are nothing but organic esters of the alcohols. These esters are much used in making fruit-syrups, ice-creams *sherbets* and in confectionery, for scenting various substances. Alcoholic solution of iso-amyl acetate which has the characteristic odour of pears is commonly used as a substitute for *pear-oil*, a solution of acetic n-octyl ester passes for *orange-essence*, iso-amyl isovalerate for *apple-essence*, a solution of ethyl n-butyrate for *pine-apple-oil* and so forth.

It is a matter of common experience that alcoholic solutions of the synthetic essences are often purchased under the impression of real flower-essences. The scent-industry has indeed undergone a remarkable revolution in recent

years. Here again the chemist has succeeded, to a marvellous degree, in deciphering the secrets of Nature's heart. She develops in flowers and plants the sweetest and most lovely perfumes which are wafted by the refreshing air and charm the human mind. Two substances deserve special mention in this connection,—ionone and attar of roses. The chemist has prepared the ionone and the attar of roses which have so great osmophoric value that a few drops would envelope a large hall in an atmosphere of violet or rose perfume; and it is a happy record that these highly fashionable flower-essences have been synthetically produced and placed on the market. It is to be remarked that the high-priced Indian *áttars* are genuine essential oils, extracted from flowers or scented woods by a laborious process of distillation or extraction, important centres of the industry being Jaunpore, Cawnpore and Ghazipore. Whether a particular sample is a pure essential oil or an alcoholic solution of the oil may be recognised by a very simple test, *viz.* by adding water to a definite volume of the substance under examination and observing the quantity of the essential oil which floats on water, the alcoholic content, if any, remaining dissolved in water.

41. Alcohol is the Basis of numerous Industries: Vast possibilities of its manufacture in India as indicated by Statistical Evidence: Necessity of Untaxed Alcohol for Manufacturing Purposes.—The alcohols are extensively made, as has been pointed out before, from starch—a staple agricultural produce of India. Some of the items of export of starchy and cellulosic Indian produces are stated in the order of their total value, *viz.* rice, wheat, raw cotton, raw jute, manufactured cotton and manufactured jute. The approximate value of the first three commodities are given *in crores* of rupees,†* noting the name of the chief Indian ports from which they are exported :—

Rice—14 (Rangoon, Burma.)
5 (Calcutta, Bengal.)
1 (Madras, Madras Presidency.)
Wheat—12 (Karachi, Sind, Bombay Presidency.)
4 (Calcutta, Bengal.)
2½ (Bombay, representing the export of the Deccan part of the Bombay Presidency.)

* One crore = ten millions.

† Rupee is an Indian silver-coin ; one rupee = 1⅓ shillings net.

Cotton— 12 (Bombay, representing the export of the Deccan part of the Bombay Presidency.)
$2\frac{1}{2}$ (Madras, Madras Presidency.)
2 (Karachi, Sind, Bombay Presidency.)

Besides the large proportion of the produces consumed in India, the export-figures give an idea of the huge quantities of raw material available for alcohol and other industries in this country.

Of the industries immediately dependent on starch, brewing stands out pre-eminent as stated before; if fermentation-industry is developed in India, numerous chemical industries may spring up therefrom. Specially trained and organising experts, sufficient capital and selection of a suitable site for the establishment of factory are important factors which simultaneously may contribute to its success; besides these, concession from or co-operation with Government is also no less an important consideration, because there is the vital question of Government license and taxation. In all countries the manufacture of strongly alcoholic liquors is made a means of raising revenue by the Government; consequently, the distilled liquor-industries are subject to constant vigilance and interference by the

excise-revenue officials and many laws are enacted presumably to prevent fraud. An excise tax which indirectly falls on the consumers, is a heavy burden on those industries using alcohol; most countries permit the use of *untaxed* "denatured alcohol" for manufacturing purposes, and without such sympathetic Government co-operation chemical industries, especially when in nascent condition, cannot thrive. It is "denatured" in order to render it unfit for human consumption. English *methylated* spirit is not impure methyl alcohol, as some lay people may think, but it contains 90 per cent ethyl alcohol, mixed with 10 per cent crude methyl alcohol. In some countries, the United States of America and Germany for instance, alcohol is denatured by adding benzene or pyridine. Wines and brandies, however, are alcoholic liquors not made from starch, but from fruit-juices which are subjected to a special method of fermentation.

CHAPTER VIII.

Manufacture of Higher Alcohols from Starch and Cellulose : Commercial Success of Artificial Rubber from them.

42. Natural Rubber may share the fate of Natural Indigo.—The manufacture of alcohols brings us to an industry which has an interesting history of its own. It is no mean triumph of synthetic chemistry in that direction of achievements which have witnessed the stifling of natural indigo, the plantation of which was extensive in many districts of India and has left behind traditions in Bengal and Behar in particular. Although the first successful synthesis of indigo was baptised in an English laboratory by W. H. Perkin, sen., its production on a commercial scale at a cheaper cost was, however, made possible on the German soil. The present European War has brought a reaction in the different phases of industrial activities, notably the coal-tar dyes ; and the Perkins in England,

who have a proud tradition for signal work on dyes, have now put forth their energies in order to revive the cultivation of natural indigo on improved system. The alcohol industry has brought us to synthetic rubber-product which is still in its infancy but has such a bright prospect that synthetic indigo may in future envy. When once the synthesis has been effected, its commercial success is only a question of time. Rubber-plantation is an extensive industry in Assam, Burma, the Strait Settlements and Ceylon and it is feared that, in no distant future, the synthetic material may capture the market and eclipse the India-rubber trade.

43. Early History of Rubber-synthesis.—The synthesis of rubber * has not its origin in any systematic attempts to synthesise that article. It is the result of accidental experiments and observations; and it is of interest to briefly review the history of rubber-synthesis and the important part that starch may play in making it a commercial success. The present account will indicate how apparently useless and unconnected pieces of chemical researches have stimulated activities in quite remote spheres and

* Pond, Review of the Pioneer Work on the Synthesis of Caoutchouc, Jour. Amer. Chem. Soc., 36, 165 (1914).

are pregnant with great industrial issues. The earliest chemical work on rubber was concerned with the destructive distillation of natural rubber which is obtained as a milky exudation, technically known as *latex*, by making incisions on the barks of rubber trees; and the ultimate synthesis of caoutchouc owes its inception to the fortunate observations made during those distillation-experiments. Greville Williams isolated a liquid of low-boiling point from amongst the products of distillation which, on analysis, corresponded to the formula C_5H_8 and he gave the name "isoprene" to the substance. This liquid, isoprene, when kept for some months, was found to have lost its fluidity owing to absorption of oxygen, and passed into a viscous substance. Then on distilling this stuff, unchanged isoprene passed over, leaving a white spongy residue. Williams concludes his observations with the significant remark :—

"When burnt, it (*i.e.* the spongy residue) exhales a peculiar odour hitherto considered to be characteristic of caoutchouc itself."

It was afterwards found that on heating isoprene, amongst others, a liquid polymer, having the composition $C_{10}H_{16}$, is produced which may be called *di*-isoprene. This liquid

has been identified, by its chemical composition, unsaturated character and other properties, with dipentene which is the principal constituent of the oil of turpentine,—thus revealing a possible source of the raw material from which rubber may be synthesised.

44. First Successful Synthesis of Rubber from natural Isoprene.—It should be clearly stated that isoprene or dipentene belongs to the class of unsaturated substances which readily form additive compounds and can be easily induced to undergo polymerisation. It was, however, soon observed that by the action of strong hydrochloric acid on isoprene and subsequent distillation, a solid residue was obtained; the residue was found to possess "the elasticity and other properties of rubber itself." This may be said to be the first synthesis of rubber, though the isoprene from which it was produced, was always obtained by distilling natural rubber. Tilden, one of the pioneers in this field of activity, made the prophetic pronouncement :

> "If it were possible to obtain this hydrocarbon (isoprene) or some homologues of it from some other and more accessible source, the synthetic production of India-rubber could be accomplished."

These words embody an idea which, in recent years, has been a source of fruitful patents in the hands of three great manufacturing companies, viz., the Bayer Co., the Badische Anilin und Soda Fabrik and the Synthetic Products Co.; and here the search after a cheaper source of isoprene, its alkyl derivatives or some requisite unsaturated hydrocarbon for the manufacture of rubber, has made the importance of starch felt in the chemical and industrial world.

45. Synthesis of Rubber from Isoprene prepared from Iso-amyl alcohol.— After a long period of laborious researches, the synthesis of rubber as a commercial success may be said to have been initiated by Perkin and Strange, aided by the substantial co-operation of Fernback and Mathews. In the process of the Synthetic Products Company, the starting material for rubber-synthesis is isoprene which is made from iso-amyl alcohol, obtained by fractionally distilling fusel oil——a mixture of higher alcohols, the supply and price of which, however, greatly fluctuate.

46. The Chemistry of the Process.— The chemistry in the process is as follows : Iso-

amyl alcohol has the following formula or one isomeric with the same—

$$\begin{array}{l} CH_3 \\ | \\ CH\text{-}CH_2\text{-}CH_2\text{-}OH \\ | \\ CH_3 \end{array}$$

which is converted into corresponding isoamyl chloride like—

$$\begin{array}{l} CH_3 \\ | \\ CH\text{-}CH_2\text{-}CH_2\text{-}Cl \\ | \\ CH_3 \end{array}$$

by the action of hydrochloric acid ; and from this mono-chloride, the di-chloride

$$\begin{array}{l} CH_3 \\ | \\ CCl\text{-}CH_2\text{-}CH_2\text{-}Cl \\ | \\ CH_3 \end{array}$$

is prepared by the action of chlorine under specially controlled conditions. The di-chloride, thus obtained, is passed through a tube filled with soda-lime and heated to 470°C, whereby it is converted into isoprene :

$$\begin{array}{l} CH_3 \\ | \\ CCl\text{-}CH_2\text{-}CH_2\text{-}Cl \\ | \\ CH_3 \end{array} \xrightarrow{-2HCl} \begin{array}{l} CH_3 \\ | \\ C\text{-}CH{=}CH_2 \\ \| \\ CH_2 \end{array}$$

The isoprene or any homologue of it is poly-

merised into rubber by adding small quantities of metallic sodium or sodium amalgam either in the cold or with the application of moderate heat, * the conversion being practically quantitative and the product known as "sodium or isoprene-rubber."

47. Search for Cheaper Material: Commercial Synthesis of Rubber from Butadiene obtained from butyl alcohol: Starch and Cellulose yield Butyl Alcohol by special method of fermentation.—The great difficulty which stands in the way of this process is the cost of the starting material, iso-amyl alcohol. Various attempts have been made for a cheaper substitute from oil of turpentine, acetylene, petroleum and coal-tar, but they do not hold out any prospect of success. Butyl alcohol has recently been found to be a promising substance for manufacturing rubber. Strange and Fernback† have devised a special method of fermenting starch and cellulose for obtaining butyl alcohol at a low cost; and practically speaking, this method

---

* Mathews and Strange, Eng. Pat., 24,790 (1910); Harries, Annalen, 383,157 (1911).

† Strange and Fernback, Eng. Pats., 15203, 15204, 16925 (1911).

of making butyl alcohol from starch and cellulose may bring out the salvation of commercial rubber-synthesis. By the employment of a certain organism, called *butylic bacillus*, it has been found possible to ferment starch and more recently, saw-dust (cellulosic matter), so as to produce butyl alcohol and acetone which are fractionally separated. The bye-product acetone which is immensely demanded for the manufacture of munitions for the sake of national defence, is sold to continental consumers at a substantial price, thus cheapening the cost of production of butyl alcohol. It is thus quite remarkable how success in one direction stimulates enterprise in quite remote industrial spheres.

48. The Chemistry of the Process.—The butyl alcohol so obtained is converted into butyl mono-chloride by the action of hydrochloric acid and then from the mono-chloride dichlorides are prepared by careful chlorination. These dichlorides, when passed over heated soda-lime, give a satisfactory yield of butadiene—an unsaturated compound, containing two pairs of double bonds :

$$\begin{array}{l} CH=CH_2 \\ | \\ CH=CH_2 \end{array}$$

Butadiene or any alkyl derivative of it, capable

of readily undergoing polymerisation, yields products which are christened "normal butadiene-caoutchouc." This stuff, according to Harries,* resembles natural caoutchouc both chemically and physically, and "sodium butadiene-rubber."

49. Introduction of Vulcanisation has greatly advanced the Rubber-industry.—The artificial rubber, however, possesses all the properties of natural rubber in regard to elasticity and behaviour towards sulphur or sulphur compounds on vulcanisation, —a process necessary in order to destroy the adhesive property of rubber and to make it elastic. It is well known that the growth of the modern rubber-industry depends on the introduction of the methods vulcanisation about the year 1846, whenceforward rubber has come to find a variety of technical use, too numerous to mention. There are two general methods of vulcanisation,—(i) Hot Process and (ii) Cold Process.

* Harries and his co-workers have been making interesting studies in "Caoutchoucs." They have found that *natural* rubber gives well-defined bromide, nitrosite and crystalline ozonides. Quantitative investigations have been made with them, including

In the "hot process" rubber is always treated with molten sulphur now-a-days, while the "cold process" consists in the treatment of rubber mainly with sulphur chloride in dilute solutions. Various chemical and physico-chemical theories have been advanced to explain the nature of the change in rubber which takes place during vulcanisation; but this is no place to enter into a detailed theoretical consideration of the processes.

50. Brief Survey of the diverse Technical Applications of Starch.—It is found from what has been said in the foregoing pages how immensely starch is used as a food-stuff in various forms, how much it has been of service to paper-manufacturers, toilet-powder-makers and laundrymen; how largely is it employed in the gum-industry and for the manufacture of grape-sugar, dextrins and alcoholic *liquers* or *cordials*; how vastly it is applied in the fermentation industries and the extensive industrial application of alcohols so obtained is well-

---

determination of molecular weights. The identity of these data as well as evidences furnished by the hydrolysis of ozonides with the corresponding experimental results from *synthetic* rubber has led them to suggest the identity of some varieties of artificial rubber—"normal" ones—with natural caoutchouc.

known. The alcohols with their bye-products have been of tremendous help in the manufacture of munitions and are so materially advancing the synthetic rubber-industry; they are the source of numerous derivatives having theoretical, therapeutic or industrial significance. It has now become a matter of history that from the time when Dobereiner first suggested the use of artificial perfumes, how marvellously the alcoholic solutions of organic esters and other compounds of good scents, containing 45 to 50 per cent of alcohol, have come into popular use.* It many be noted here that even the fragrant pomatums are principally nothing but perfumed fats, animal or vegetable. So starch is the mother of such a vast number and variety of industries, big and small.

We now leave the subject of the bearing of starch on modern chemical industries by appending a chart for clear and easy reference, and pass on to the chemical technology of cellulose.

---

* The well-known Eau-de-Cologne which is, at the present day, an alcoholic solution of a mixture of nearly a dozen of mainly synthetic essences is made, not in Cologne alone but in India, Japan or any other part of the world.

STARCH. $(C_6H_{10}O_5)_n$

- Most staple of animal foods—
  - Barley powder, sago, arrow-root, vermicelli, toilet powder, etc.
- Size in paper manufacture,—stiffening and glazing material in textile industry and laundry, etc.
  - Extensive use in condensed milk manufacture.

- Ordinary Starch.
  - Fermentation industry.
    - Ethyl alcohol.
      - Compounds having industrial, therapeutic or theoretical significance *viz.* vinegar, chloroform, iodoform, ether, antifebrin, sulphonal etc.
      - Artificial perfumes including fruit and flower essences
    - Fusel oil : Iso-amylalcohol
      - Synthetic rubber.
  - *Strange and Fernback Fermentation.*
    - Butyl alcohol → Synthetic rubber.
    - Acetone
  - Grape-Sugar, dextrins.
    - Alcoholic *liquers* or *cordials*
  - Xylodine or white gunpowder, oxalic acid, patent gums etc.,.
- Soluble Starch, patent starches, etc.

CHOUDHURI, CHEM. IND.,
Starch Chart,
1915.

CHAPTER IX.

Textile Fibres: Their Scientific Diagnosis, Identification for Commercial Purposes and Manufacture.

It should be borne in mind that the industrial application of a substance depends primarily on its chemical and physical character. The technical applications of cellulose are so varied and so extremely diverse in scope,—the products so interesting, so enjoyable and useful and others again so dangerous, that any branch of it may require a decent volume by itself. Only the general technical bearings of cellulose will be dealt with at some length without freely going into technological details. With this end in view, it will be necessary to summarily consider some of the subjects.

51. Different Classes of Textile Fibres.—Cellulose, as has been mentioned at the outset, is very largely used in the textile industries which, strictly speaking, although cannot come under chemical technology, involve some important chemical operations in the preliminary

stages of the fibres and have given rise to some important chemical bye-industries. Textile fibres are, however, classified into vegetable, animal and mineral, according to their source. In textile industries only the first two are employed; mineral fibres, the chief which are asbestos, slag-wool and glass-wool, are not subjected to a textile process of any importance. Cotton, linen and jute belong to vegetable fibres, while wool and silk come under animal fibres, as has been said before.

52. Distinction between Vegetable and Animal Fibres from Physical and Chemical standpoints.—There are marked differences in the physical structure and chemical composition of the two kinds of fibres, a reference to which has already been made.* The methods of distinguishing vegetable fibres from wool and silk as well as fibres of the same class from one another, depend upon the differences in their physical and chemical properties.

53. Structural Identification of Fibres by Microscopic Examination.—A microscopic examination of the fibres reveals the fact that they are structurally very

---

* Vide pp. 9, 19-20 of this book.

different. The vegetable fibres are composed of hollow cells, fairly long, each cell having a central canal or *lumen*, as it is called, running through it. In cotton, the fibre consists of a single cell, whilst in jute and linen the cells are grouped together in bundles to form the fibres. Amongst the animal fibres, wool has the most complex structure, being made up of cells of three different kinds; silk, on the other hand, may be said to be devoid of any definite structure. The fine nascent thread, as it issues out of the silk-worm, consists simply of a long double cylinder.. The nature of the fibre of which a texture may be woven can be identified with the help of a microscope.

54. Some Chemical Tests for readily Detecting whether a Fibre is of Vegetable or Animal Origin.—Some simple tests may be prescribed for determining the nature of a fibre. Of them, the following may be readily applied :—

(1) The animal fibres—wool, silk or alpaca—are at once distinguished from the vegetable fibres—cotton, jute, linen or flax—by the fact that the former being amino-acids are dissolved in caustic soda solution, while the latter are left behind.

(2) The animal fibres, on being singed, give off a smell like that of burnt feathers ; and when burning in a candle-flame and taken out, the fire is immediately extinguished, a black residue of carbon being left ; whereas artificial silks or vegetable fibres do not give off smell like burnt feathers, continue to burn when taken out of the flame and also leave no carbonaceous residue when extinguished.

(3) Wool and silk etc. are coloured yellow by strong nitric acid (sp. gr. 1·3) ; cotton, jute etc., on the other hand, are not coloured but oxidised.

(4) A solution of mercury in nitric acid, known as Millon's reagent, colours the animal fibres intensely red and on adding a solution of sodium sulphite, the red colour changes into black ; while cotton, jute or linen is not acted upon by this reagent.

55. Examination of a Mixed Texture. —It is often commercially necessary to find whether a sample is a pure or a mixed fabric ; and physical and chemical examinations are resorted to for this purpose.

1. Physical Method :—When a texture is supposed to be a mixed fabric, made of both animal and vegetable fibres, chemical tests are

resorted to in addition to microscopic examination, which has already been described in paragraph 53. A small microscope, known as "linen-prover", is sold for examining and diagnising the character of such a fabric.

2. *Chemical Method*:—In addition to the four above tests, the following specific reactions are conveniently applied. It has been found that a solution of ammoniacal copper oxide in excess of ammonia dissolves silk first and cotton next, wool remaining insoluble. When, however, wool and silk only are present in the texture, the latter may be dissolved by successive treatment with nitric acid and ammonia, while wool is left behind. Sodium nitro-prusside gives undoubtedly the most delicate test for distinguishing between wool and silk in their solution in caustic alkalis ; with wool, the nitro-prusside solution immediately produces a violet coloration owing to the presence of sulphur in wool. In the present place, we are principally concerned with the vegetable fibres which belong chemically to the cellulose-class.

The vegetable fibres for use in spinning must be firm, pliable, easily divided and capable of withstanding bleaching operations when neces-

sary. To ensure the best quality of the fibre, the chemist has to examine the soil and select proper fertilisers. It will be presently found that although textile industry does not belong to chemical technology, it is intimately connected with some important industries, indispensible at the present day.

56. Extraction, Quality and Variety of textile Cotton.—Of all the varieties of cellulosic fibres, cotton is the most important. It is the fruit of a plant which is extensively cultivated in the tropics. The fruit consists of a cup-shaped calyx, enclosed in a three-clept outer calyx and containing a soft white down. In order to separate the downy cotton from the seed, it is subjected to a process, termed *ginning*. The down is kept separate from the seed when packed for transit, as it may become oily and unfit for textile use if put in contact. The quality of cotton is determined by its smoothness, fineness, strength and length. Cotton is subjected to various processes of purification, carding and drawing in order to convert it into spinning fibres and is named after its place of origin *e.g.* American, Varginian, Egyptian and Indian cottons.

57. Some Special Kinds of Cotton-textures.—Of some special kinds of textures

in which cellulose-fibres are employed, may be mentioned calico-prints, shirtings, cambrics and muslins which are glazed linens ; drills, satins and fustians which have cross-cords, and a variety of cotton-velvet which is largely manufactured in Manchester.

58. Indian Method of Jute Extraction: Chemistry in the Process.—Now we come to jute. It is interesting to briefly describe the method of making jute fibres in Bengal. The cultivators cut the jute-plants during the rainy season (August-October), tie them up in bunches and often keep them on the field until the leaves fall off. The fibre lies under the bark of the plant, surrounded by a gummy substance which consists, according to J. Kolbe, mainly of pectose and must be removed in order to make the fibre fit for textile use. For this purpose, the plant now undergoes a wet process, called *jág*, during which it is arranged in heaps under water for a period which depends chiefly on the character of the water and firmness of the bark. This process of "softening" or "rottening" is usually complete in about two weeks and a chemical change is involved in it. It appears that both putrefaction and fermentation are set up, the former being

easily recognised by the bad odour of the *jág* and its water; while during the latter, pectic fermentation probably takes place in course of which pectose or pectin is converted into pectic acid which, with other impurities, separates out in the water. The rotten plants are now taken out and the central woody part removed by "fleecing out" the adhering softened barks by what may be called "thrashing" or "batting" and finally purified by washing. The jute-fibre is then hung up to dry in the sun.

59. Discussion of the Process.—The process is, however, not very sound from scientific point of view. For keeping the plants in bath for a long period, the fibres are affected in the following ways :—

(*i*) The strength of the fibre is liable to be weakened.

(*ii*) Its colour becomes a little dark or brownish.

(*iii*) As all parts of the plant are not uniformly softened, the impurities, including incrusting bark, are not thoroughly removed.

This Indian system, however, is cheap and economical, but owing to its increased cultivation at the present day, its exaction, along with other

agencies, on the life of the people in the jute-area is by no means inconsiderable.*

60. Manufacture of Flax.—The manufacture of flax is practically similar to the Bengal-process of jute-extraction. There is mainly this difference that in the Western countries the flax-fibre is subjected to purification by hot cleansing in a dilute alkaline or sulphuric acid bath which yields the best results.

61. Similarity in the Composition of Cellulose-content in the Fibres.—The composition of the cellulosic contents of wood, cotton, jute and flax is practically the same, as is evident from the following analytical results :—

	Wood	Cotton	Jute	Flax
Carbon ...	43·87	43·30	44·12	43·68
Hydrogen ...	6·23	6·40	5·72	6·21
Oxygen ...	49·90	50·30	50·16	50·11
	100·00	100·00	100·00	100·00

62. Some Technical Uses of Vegetable fibres.—The vegetable fibres as such are largely used for making textiles, ropes and

* Vide foot-note p. 3

fishing nets.* Jute has besides found extensive application in the manufacture of gunnies and cheap warm fabrics ; while cotton, impregnated with various disinfectants, is largely used in surgery ; and among the various substitutes for absorbent cotton now being employed in Europe, are "lignin" made of pine-cellulose, and "cellulose wadding" made from chemical wood pulp, and "bog moss." † It is to be noted that *kapok* or "vegetable wool", obtained from a tree in Ecuador and the Dutch East Indies, is extensively used for mattresses etc. in the United States ‡.

63. Cotton-industry as the Parent of many Bye-industries.—We shall consider cotton as the representative of cellulosic fibres and now proceed to see in how many and varied directions it has found industrial applications and how it has led to the establishment of different kinds of bye-industries.

---

* India has the monopoly of jute, the area under cultivation being roughly 4,829 square miles. An idea of its huge production may be had from the fact that the total value of jute in rupee-coins, if stacked, would make eighty piles as high as Mount Everest, and, if placed side by side, would make three belts round the world. *Cf.* G. S Eddy's Statistics, S. C. Mag., Jan., (1916).

† Commerce Reports, U. S. A., Sept., 1306 (1915).

‡ *Ibid.*, 1294.

The relation of the industrial chemist to the cotton-industry is very great at the present day.* At the time of plantation, he has to study the soil and prescribe the fertilizers necessary to ensure the best types of fibre; in the ginnery the chemist finds the cotton-seed and from it produces the oil which bears its name, about 25 lbs. of the seed yielding 1 lb. of the oil †; in the soap-industry he has utilised the waste from refinery of the cotton-seed oil and has recoverd glycerine,—a substance of great chemical significance. He has hydrogenated the refined cotton-seed oil and has thus produced a vegetable fat, so largely demanded as a cooking material and also in soap-manufacture. ‡ Following the pressed seed of the mill, the chemist has waylaid the hulls and has proved them to be a valuable fodder for cattle; and more than this, he has demonstrated their value as manure and paper-stock.

* Dannerth, Jour. Ind. and Engin. Chem., Jan., 75, (1916).

† U. S. A. exports alone of cotton-oil exceeded 35,000,000 gallons in 1913.

‡ A market is desired in India for vegetable tallow, formerly shipped to Antwerp, for making candle and soap, and for use as an edible fat. Commerce Reports (Consular), U. S. A., Jan., 335, (1915). Bombay Presidency which possesses dozens and dozens of cotton-ginning factories should now pay more attention to the important bye-industries.

Besides these uses, cotton-meal is itself now-a-days a well recognised feedstuff, and the "oily hogs" which are produced by a strong diet of this material are seen in almost every pork-packing plant in America.

64. Manufacture of Pure Cellulose: its Character and Application.—It has recently been discovered that **pure cellulose** * made from wood does not rot even when buried under ground, because all the incrusting matter with which it is associated in nature is removed during purification by the digestion-process. Pure cellulose may be said to be indestructible, except by such drastic treatment as by fire or boiling with acids. Its application may range from the manufacture of cellulose-coffins to cellulose-whiskey, from steamer steward's bad weather-basins to fine cellulose-suits which are more strong and durable than ordinary cellulosic stuffs. A London firm has already launched upon making textiles of various description from pure cellulose with nice shades of colour.

65. Cellulose Revolutionises the Industry of Artificial Lights: Manufac-

* Raitt, Recent Progress in Cellulose Textiles, Indian Forester, 1916.

ture of Welsbach Mantles.—It is important to see how cellulosic fibres have found interesting application in revolutionising the industry of "artificial lights." For centuries attempts have been made to utilise the light emitted by some substances heated to incandescence; and the present knowledge of the subject dates from about the year 1880, when Dr. Carl Auer von Welsbach began his researches on the rare earths elements. He observed that threads of cotton, impregnated by being dipped into a solution of the nitrates of the rare earths, leave after ignition a coherent coating of their oxide which glows brightly when heated. Varieties of substances, viz. asbestos, platinum and bamboo-filament for mantle-making and numerous combinations of mixtures for mantle-impregnation have been proposed and patented from time to time. But it was only in 1891 when Dr. Carl Auer, in course of his examination of a quantity of impure thoria, found that the cotton-mantle, impregnated with nitrate of this impure thoria when heated emitted a light which, however progressively diminished in intensity as the thoria was gradually further purified, that the success of the gas-lighting industry became practically assured. It was soon discovered that the presence

of a *small but definite* quantity of ceria acts as the "excitant",* extraordinarily raising the light-giving power of the cotton "stockings", as the mantle is technically called. It was further observed that any deviation from this precise proportion of thoria to ceria would remarkably decrease the emissive power of the mantle. And Von Welsbach patented† his "Auer mixture" which consists of a solution of the nitrates of thorium and cerium in such a proportion as to leave a coherent ash of their oxide on the mantle when ignited, approximately in the proportion of 99 per cent. of thoria and 1 per cent. of ceria. This industrial application of thorium and cerium which are obtained as a bye-product of the radium-industry has served to stimulate the study of the rare earths, and is a striking proof how purely scientific researches respond to the appeals of industry in quite unexpected directions. The significance of the discovery of "Auer mixture" will be best seen from the following diagram.

* Various theories, including Catalysis, have been advanced to explain the extraordinarily high light-giving property of this mixture. Vide Fischer, Der Auerstumpf; Ahren, Sammlung, XI, 1906.

† Moeller, Eng. Pat., 124 (1893).

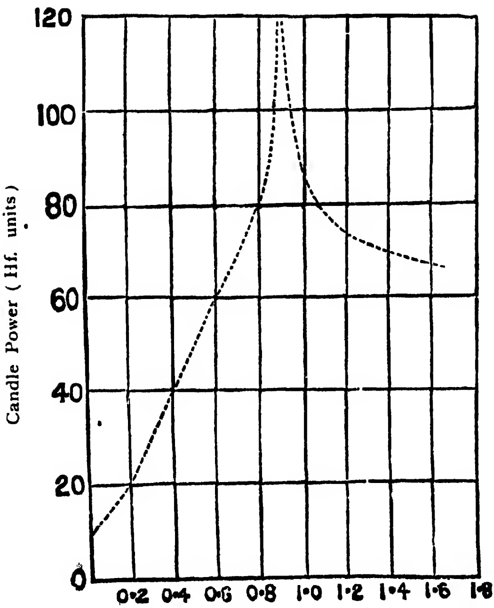


Diagram * Showing the Effect of Percentage of Ceria.

66. Drawbacks of Cotton-mantles: Other Forms of Vegetable fibres discovered as Suitable Substitutes.—But even now the gas-lighting could not compete

* Drossbach, Jour. Gasbel., 352 (1898).

with its formidable rival, electric lighting. As threads of cotton are made by twisting a very large number small fibres, the mantles suffered from the serious objection of shrinkage and of developing little volcanoes due to torsion in the mantle-thead after use for only a hundred of hours ; consequently, the Welsbach mantles became fragile and fell to pieces. It was now realised that long fine homogeneous fibres and means of preventing the fragility of the mantle after burning so as to render it fit for transport, were factors essential to secure the effeciency of mantles and success of the gas-lighting industry. The remedy for the fibre has come from China-grass or ramie, a kind of long grass which is largely grown in India (Assam), China and Italy. Another important source, at the present moment, is artificial silk out of which long continuous thread can be spun,—a subject which we shall take up in a subsequent chapter. Although the manufacture of artificial silk was first achieved in France, it was however successfully applied to mantle-making in Germany ; but this application is very limited, as by far the greatest quantity is produced from ramie fibre. In the United States even to-day a considerable number of mantles is made from cotton. As regards the second

drawback of fragility, it has been successfully removed by a process known as collodinisation which consists in treating the finished mantle with a solution of lower cellulose nitrates (collodion). It is thus remarkable how vegetable fibres as such and chemically treated, have been of service in bringing out the salvation of the long-struggling gas-lighting industry by putting it on a stable basis.

CHAPTER X.

Cellulose the Basis of Paper-making Material: Numerous Technical Uses of Paper.

The manufacture of pulp for paper involves certain chemical processes indispensible at the present day. Paper consists of cellulose fibres made into a coherent sheet, and the raw materials for paper are cotton or linen rags, esparto, straw, hemp, jute, and the most extensive supply to-day is wood-pulp. Details of the technology of paper are, however, not within the scope of the present work which has in view to outline how cellulosic materials have been of great service in advancing human progress and civilisation, and diffusion of learning from the dawn of creation onwards, and how the extensive application of paper in various directions has led the chemist to tap new sources of raw cellulosic material for the manufacture of paper.

67. An Outline of the History of Paper-making from the Earliest Times. —The history of the paper-making industry from

the earliest times to the present day is an interesting one. In very ancient times, men engraved some signs upon stone, wood and metals, and by this means they handed down any records to posterity. In India birch bark, palm leaves and *sachi* leaves were largely used for writing purposes. About 600 B. C. the Egyptians made the famous *Papyrus Cyprus* from the Cyprus grass which was universally considered as a luxury for writing in Europe during the middle ages; this was, however, supplanted by cotton cloth which was much valued as a parchment mainly on account of its durability. The invention of paper, according to Menon, is assigned to the year 105 A. D. * It was made in Tibet in the middle of the eighth century A. D., and what was known as "Nepal paper" is the oldest recorded sample. The manufacture of rag-pulp seems to have originated with the Arabs, although the first reference to it is at Nuremberg in Germany in 1390. Later on, a paper-mill was erected in England by Sir John Spielman in 1588 near Dartford, for which he was knighted by Queen Elizabeth. But there is evidence to believe that the Chinese were the pioneers in using vegetable pulp

* Menon, The Paper Industry, N. F. Ind. Assoc., Feb., 1916.

for paper-making. The old hand-made paper, however, has now-a-days been supplanted by machine-papers. Since the introduction of pulp-paper, the paper-industry has made marvellous progress.

68. Recent Advancement: Tapping New Sources of Raw Material.—It has been experienced more than once that the printing press has been threatened with shortage of pulp-making material. As the consumption of paper has been phenomenally increasing, search has been made to tackle fresh resources of raw material, and promising rich sources have been found in some species of grass and wood, all soft wood being fit for pulp-making. The Indian mills manufacture their paper from rags, jute, straw, etc., and owing to the scarcity and dearth of these articles, *bait* grass has been successfully used for the last twenty years. * Recently *sabhai* grass has also been worked to yield a good quality of pulp.

* The decision of the Swedish Government to prohibit the export of wood-pulp (1915) has called immediate attention to vast stores of raw-materials all over the world which have been hitherto of little or no economic value. The United States of America are making efforts to utilise their neglected resources in this direction. The British Empire is also tremendously rich in pulp-producing materials. In Canada and Newfoundland huge areas of soft coni-

69. Processes for making Mechanical and Chemical Pulp.—All materials suitable for paper-making are first converted into pulp which consists in effecting the cellulose-fibres free from adhering matters and reducing the material to a minute state of subdivision, so as also to separate, more or less completely, the individual fibres; and certain chemical processes are involved in this connection.

Wood-pulp from which the largest quantity of paper is manufactured at the present day, is of two kinds, mechanical and chemical, named according to the process employed in making it. The **mechanical pulp** is produced by directly disintegrating large sticks of wood by forcing them against a revolving wheel over which

---

ferous woods, such as fir, pine and spruce, which produce a pulp of high quality, are still untouched. In Assam, Central and Northern India, enormous forest-tracts are covered with grass, at least half a dozen different types of which yield pulp of first class quality. In Mysore also the forests already explored would yield annually about 60,000 tons of grass for pulp-making. Large tracts of bamboos are at the same time available in various parts of Lower Burma, Southern India and Sikkim; the Himalayan forests still remain unexploited, while the supply of *elephant* grass in Uganda is practically inexhaustible. How serious have been the attempts in this direction may be seen from the fact that a factory is already at work at Trinidad, turning out pulp from sugar-cane residues hitherto used only as fodder and fuel.

a stream of water continuously plays for washing the crumbled matter. The pulp prepared by mechanical proces contains lignin and resinous matters which turn brown when exposed to light. Paper made from this pulp is not strong, as fibres are very short and do not mat together so well. It is used for making cheap stuff like news-paper.

The **chemical pulp** is produced from wood mainly by three different processes, namely, the *soda process*, the *sulphate process* and the *sulphite process*. Brief description of these processes is given here.

70. Manufacture of Soda Pulp and Utilisation Soda Waste Lyes.—In the soda process for making wood-pulp, soft timbers, after removing their bark, are cut into very small pieces which are washed, and then transferred into digesters. The chips of wood in the digesting vessel are covered with caustic soda solution of some known strength, and heated for about eight hours. During this "cooking" the non-cellulosic matters are acted upon by caustic soda, and the resulting organic acids serve to neutralise nearly all the alkali, major quantity of which is recovered and used again in "cooking".

Caustic soda has direct action on cellulose, and the value of this action will be seen in a subsequent chapter on the manufacture of artificial silk. Owing to this action, a portion of cellulose remains dissolved, while the pulp-fibre becomes weak and soft. Patent has, however, quite recently been taken out for producing methyl alcohol and acetone from the waste liquor of soda-pulp by subjecting the concentrated liquor to destructive distillation at 300° in the presence of a catalyzer such as "black ash." *

It is thus evident that, in India as elsewhere, really successful and economic development of chemical pulp-industry is intimately connected with the establishment of alkali manufacture which, in itself, is also a great exponent for determining the success of various other important chemical industries.

71. The Sulphate Process of Making Pulp and Economic Utilisation of its Waste Liquor.—This process consists in boiling chips of wood, generally spruce and fir, with a solution of sodium sulphate containing a small quantity of caustic soda and sodium carbonate under pressure for about 32-35 hours.

* White, U. S. Pat., 117983 (1916).

In this process a good yield of pulp with strong fibre is obtained.

Various processes for utilising the residue from the sulphate pulp which was until recently thrown as a waste material, have been devised. In Germany the waste liquor is neutralised with lime, filtered through coke, and is then evaporated to a nearly dry pitch-like resin known as "Zellpech".* This material is used as a binder in coal-briquets, ore-briquets as well as in making artificial stone and moulding sand. "Zellpech" is also used for filling cotton goods and impregnating sail-cloths, cords and nets. But a more important application of the sulphate liquor has recently been found in the manufacture of alcohol. In Sweden alcohol is being successfully made from the waste sulphate liquor.†

72. Manufacture of Sulphite Pulp and Industrial Utilisation of the Sulphite Waste.—In this process of manufacturing pulp, the timber, after being cut into small chips as in the soda and sulphate processes, is heated under pressure with a solution of sulphurous acid or, more generally, with a mixture

* Commerce Reports, U. S. A., Aug., 782, (1916).

† *Loc. cit.*

of calcium and magnesium bisulphite which is commonly made by passing sulphur dioxide through towers packed with dolomite over which water trickles. The chemical reactions involved in the sulphite process are complex and chiefly as follows. The acid calcium sulphite present in the bisulphite liquor is unstable, and gives rise to free sulphurous acid which, at the first stage, probably hydrolyses the wood into free cellulosic matter, complex organic acids, aldehydes and incrusting matter under high temperature and pressure of the digesting vessel. Several secondary reactions proceed simultaneously, resulting in the formation of tarry matter and organic bisulphite compounds with the aldehyde which are, however, soon decomposed by the organic acids, forming soluble calcium and magnesium salts and setting free sulphurous acid gas. The pulp produced by this process is bleached by the sulphurous acid, but the original colour of the pulp often returns afterwards; and for permanent whiteness the pulp, after thoroughly washing off bisulphite, is bleached with chlorine.

The sulphite pulp has long and strong fibre. It is often used unbleached and is better than soda pulp.

The liquor from the sulphite pulp as that from other precesses, contains much dissolvéd cellulosic and other organic matter, only 45 per cent of the original weight of wood being converted into pulp. The problem of economic utilisation of the waste liquor has received the attention of industrial chemists and paper-makers for a long time, and we have found some of the channels in which the soda and the sulphate lyes have found technical application. Various suggestions * have been made that the liquor may furnish material for manufacturing oxalic acid, pyroligneous acid or alcohol ; and we shall see how industrial researches have brought about the salvation of the waste liquor by its successful commercial utilisation partly in the manufacture of alcohol (sulphite spirit) † and quite recently, in the production of sulphite coal or coal-powder for fuel. The residue from the sulphite pulp is about 55 per cent of the original wood subjected to pulp-making ; and of this, only 2 per cent is accounted for by alcohol-manufacture at the

---

* Griffin and Little, The Chemistry of Paper-making, 271(1894). Hubbard, The Utilisation of Wood-waste (1915).

Beveridge, Utilisation of Sulphite-lyes, Jour. Soc. Chem. Ind., 35, 563 (1916).

† Oman, Fermentation of Sulphite Wood-pulp Waste-lyes, Papierfab., 13, 534 and 553 (1915) ; Zeit. angew. Chem., 28, II, 564.

present day, so that more than 50 per cent of the total weight of wood remains unused. Strehlenert * has invented a process which has started operation at the Greaker Cellulose Works (Sweden) with a capacity of an annual outturn of some 6,000 tons of coal. It has also been recently proposed to convert the sulphite lye into cattle-feeds. †

73. Manufacture of Paper from Pulp.—The process of paper-making is mechanical in character and does not come strictly under the province of chemical technology. It consists in matting the cellulose fibres into a coherent sheet. In order to give the paper what is called body, weight and smoothness, some *filling* or *loading* material is used with the pulp. The loading materials generally employed are barium sulphate, gypsum, kaolin and talc, etc. When it is intended to make coloured paper, the desirable colouring matter is mixed generally with the pulp. For white paper, however, the pulp is bleached before being made into sheet.

---

* Sulphite Residue as Fuel (Strehlenert), Chem. Trade Jour. *ref.* Jour. Ind. Eng. Chem., 8, 1070 (1916).

† König, Treatment and Utilisation of Sulphite-cellulose Waste-lyes, Zeit. Nahr. Genussm., 31, 171 (1916); Jour. Soc. Chem. Ind., 35, 960.

Paper is known under various commercial names and may be (*a*) sized, as for instance various kinds of writing paper, and (*b*) unsized or bibulous, as an example of which blotting paper may be mentioned, and also (*c*) half-sized, which is given different shades of colour and is mainly used as packing paper. The process of sizing consists in coating the surface of the paper with some material which prevents the absorption and spreading of ink. Paper sometimes undergoes a process called "calendering" in which it is passed through hot revolving cylinders in order to give the paper smooth and glossy finish. *

74. Methods of making Parchment Paper, Vulcanised Fibre, and Willesden Paper, Cloth and Canvas.—Paper is subjected to some special processes, involving chemical reactions, for making parchment paper, the so-called vulcanised fibre and Willesden paper. **Parchment paper,** also called vegetable parchment, is made by dipping unsized paper into strong sulphuric acid mixed with half its volume of water and a little glycerine. The paper is quickly removed, copiously washed

* In trade the symbols "S & C" signify the words 'sized and calendered'.

with water and dilute ammonia, and dried. During this treatment the cellulose of the surface is converted into amyloid* which closely cements the fibres together. A strong solution of zinc chloride † has also parchmentising action on paper; and this action is made use of in the manufacture of what is known as the **vulcanised fibre.** ‡ For this purpose, paper is treated with a solution of zinc chloride whereby the cellulosic surface is gelatinised when several sheets are matted together; the zinc salt is then washed and the thick sheet is made waterproof by treatment with "nitrating" acid. Quite recently however, a patent has been taken out for the manufacture of waterproof paper. § While **willesden paper** is made by subjecting paper to the action of a strong solution of Schweitzer's reagent. ** During this process cellulose of the surface is turned sticky, owing to the formation, according to Piest, of cupramine cellulose compounds by the replacement of the hydroxylic hydrogen in cellulose by copper and the amino

* Hoffman, Annalen, 112, 243.

† Wynne and Powell, Eng. Pat., 16805 (1884).

‡ Jour. Soc. Chem. Ind., 552 (1897).

§ Kindleberger, U. S. Pat., 1126783 (1915).

** A solution of copper hydroxide in aqueous ammonia is known as Schweitzer's reagent.

group—NH_2.* Several sheets, similarly treated, are pressed together, the cupramine cellulose forming a waterproof coating. Willesden cloth or canvas is also prepared in the same way. A more interesting application of the action of this reagent on cellulose will be found in the manufacture of artificial silk.

75. Manufacture of Artificial Boards.—The principle underlying the last process is utilised in the manufacture of **artificial board.** A sheet of paper is left for a short time in contact with "ammoniacal copper" solution, so that the fibres are superficially attacked. This, when passed between rollers and dried, becomes totally impervious to water, and its cohesion is not affected by extremes of temperature. Two sheets, thus treated, mat together firmly, and with a sufficient number of this, artificial boards are produced. A variety of materials are largely manufactured in this way at the present day and are useful for efficient roofing and other purposes. †

It is also interesting to note that impermeable cardboard and pasteboard suitable for making

* Piest, Die Zellulose, 1910.

† Wright, Jour. Soc. Chem. Ind., 121, (1884).

cartridge-holders, parts of shoes, military caps and other articles, are manufactured by heating wood-pulp with a solution of resinous glue and colophony in requisite proportions. *

76. Use of Paper in making Paper-towels, Handkerchiefs and Glasses.—Besides these chemico-technical applications, paper or paper-pulp has found uses, though not of any chemical bearing, in so many other directions that it is meet to make reference to some of them here. It is interesting to note that paper-towels and paper-handkerchiefs are largely coming into use. Even round drinking cup made of one piece of paper, without any gum, paste, paraffin or other objectionable matter, is widely used in offices and factories, hospitals and public institutions, theatres and clubs, hotels and restaurants. †

77. Manufacture of Fire-proof Writing Material.—It should be mentioned here that the article, generally known as **fireproof paper** is not a cellulosic stuff, and is made of "true asbestos." It has, however, been recently found that crysotile fibre, when combined as pulp at 100°C with white or lightly tinted

* Serebrianyj, Eng. Pat., 10599, July, 1915.

† American Exporter, June, 80 (1915).

precipitated compounds of metals, yields a paper which stands the "fire test" well. * As has been seen before, pure cellulose does not rot even when kept buried under earth and is practically indestructible, except by such drastic measures as by fire or boiling with acids and caustic alkalis. It is not improbable that, in future years, indestructible paper made of pure cellulose which would last for ages may be placed on the market.

78. Papier-mache' for Album-covers, Inkstands, Blotting books, Paper-knives and Battery-cells.—Before concluding this chapter, reference should be made to an interesting pulp which is now largely made from old paper by treating it with concentrated lime-water and gum, or starch-paste. The pulp so prepared is technically known as **papier-mache'**, and is used for making fancy goods, such as covers for albums, inkstands, blotting books and paper-knives. It is also used for making cells of galvanic batteries. For these purposes, the pulp is first pressed into a desirable form, coated with linseed oil, then baked at a high temperature and is finally varnished. Some-

* Myers, Jour. Ind. Eng. Chem., 8, 888 (1916).

times the pulp is mixed with clay or sand for special technical applications.

79. Industrial Possibilities for Pulp and Paper manufacture.—It has thus been found how vast a field of industry and bye-industries is covered by pulp and paper manufactures. A very large number and variety of technical applications of cellulosic material, reviewed in this chapter, have proved to be commercial success; numerous other chemico-technical; applications of the nitrate and acetate of cellulose made from purified wood-pulp or cotton we shall come across in the next chapter, and many more economic and industrial developments are expected in near future. And India, rich in her vast resources of forest timber, grass and bamboo, (*q. v.* pp. 94 and 95, foot-note) fit for turning out high grade pulp, should take an important part in the industrial activities of the world in these directions for supplying the needs of modern civilisation, aided by judicious scientific research and efficient organisation.

CHAPTER XI.

Manufacture of Artificial Silk: its Effect on Gas Mantle and Natural Silk Industries. Technical Uses of Cellulose Acetate.

80. Co-operation between Science and Industry.—After the discovery of cellulose nitrates, commonly well-known as nitrocellulose, by Schönbein and Böttger in 1846, many attempts have been made to produce a substitute for silk from them. The history of artificial silk industry, however, dates from the year 1890 when Count Chardonnet first introduced his method of making substitutes for silk. Apart from the process using cellulose nitrates, various other methods depending on some special treatment of cellulose have subsequently been discovered. The history of the development of this industry is a record showing how curiously isolated facts of apparently academic interest and unconnected discoveries of different persons at different times have been seized and forged into a systematised branch of an industry, adapted to

the needs of mankind.* It is a history of the remarkable co-operation of Science and Industry, illustrating the truth of the statement that the pure science of to-day is but the technology of to-morrow.

81. Processes for making Artificial Silk.—There are chiefly five processes for manufacturing substitutes for silk at the present day, namely, the *Chardonnet process* (1890), the *Mercerisation process*, the *Viscose process* (1893), the *Acetate process* (1894) and the *Pauly process* (1900). Each of these will now be taken up.

82. Chardonnet process of Manufacturing Silk-substitute from Cellulose nitrates: its Advantages and Disadvantages.—The raw material used in this process is cotton or, more recently, purified wood-pulp which is treated with a mixture of sulphuric and nitric acids, the latter of which replaces some hydroxyl groups in the cellulose molecule. During this reaction a mixture of mainly tri-, tetra and penta nitrates of cellulose, known technically by the name pyroxylin, is produced. The cellulose nitrates are washed free from any trace of acid; and after drying, these

* E. Fischer, Chemical Research in its Bearings on National Welfare, Jan., 11, 1911.

lower nitrates are dissolved in the smallest quantity of alcohol and ether.* The uniform solution so obtained is forced through fine glass-capillaries into water which produces instantaneous coagulation ; more recently, however, they are passed through a chamber of hot air which causes the evaporation of the solvent, producing threads sufficiently tough to weave.

The highly inflammable character of the substance renders the resulting fabric unsafe. To remedy this drawback, it is subjected to a process of "denitration" by means of a solution of ammonium sulphide. The denitrated silk is now largely used in the mantle-industry. The thread has also the advantage of possessing superior attraction for dyes. In appearance it bears close resemblance to natural silk, with this exception that it burns a little more freely. People may often buy Chardonnet silk under the impression that it is the genuine article of animal origin.

83. Manufacture of "Mercerised" Cotton or Cotton-silk.—The action of cold concentrated solution of caustic alkalis on cotton is made use of in the manufacture of what is known as "mercerised cotton", named after its

* Cellulose hexanitrate, known as gun-cotton, is insoluble in alcohol and ether. For its technical application, see next chapter.

discoverer John Mercer. The cotton fibre is naturally flat and spirally twisted ; but on treatment with alkali, it is found to be cylindrical and straight, as the central canal or *lumen* practically vanishes. The fibre now becomes translucent with a silky appearance and has also greater affinity for colouring matters than that of the natural fibre. In trade it often passes under the name of "spun silk" or more commonly, "cotton-silk."

84. Viscose process of making Artificial Silk : Merits and Demerits of the Product.—It has however been subsequently found that if the process of "mercerisation", as treating with caustic soda solution is called, is carried further, the cellulose swells up to a gelatinous, transparent mass which remains insoluble in water. In 1892 the English authorities on *Cellulose*, Cross and Bevan, made the important discovery that if cotton is treated with a 15 per cent solution of sodium hydroxide, the resulting mass, after being squeezed, easily takes up carbon bisulphide when submitted to its action in a closed vessel. The cellulose xanthate which is thus produced may be represented by the empirical composition *

$$NaS.\ CS.\ O.\ C_6H_9O_4,\ NaOH$$

* Beltzer, Zeit. angew. Chem., 21, 1731 (1908).

This substance now completely goes into solution in water, producing a transparent uniform syrupy solution which led Cross and Bevan to christen it by the name "Viscose" or "Viscoid." By forcing this viscous product through fine platinum jets into solution of ammoniacal salts, fibre is obtained out of which a texture closely resembling natural silk is woven. *

The cheapness and the simple method of manufacture of artificial silk by the Viscose process give it so great an advantage over the other rival methods that it may replace not only the other substitutes of silk but natural silk as well. Viscose silk is very suitable for making incandescent gas-mantles which will be considered later on.

85. Manufacture of Silk from Cellulose acetate : Quality and Use of the Fibre.—Recently however, numerous attempts have been made for utilising some organic esters of cellulose in the manufacture of textiles ; and the production of waterproof artificial silk from cellulose acetate † has now been accomplished on a commercial scale. Cellulose acetate is at

* Cross, Bevan and Beadle, Ger. Pat., 70999 (1893).

† Cross and Bevan, Eng. Pat., 9676 (1894).

present prepared for this purpose by treating purified cellulose with a mixture of acetic anhydride and acetyl chloride or, more recently, with acetic anhydride and a little concentrated sulphuric acid at 60°—70°C. The acetate smoothly goes into solution in acetic acid, and when passed through jets into water yields a fibre which is then washed and dried. The process has been greatly improved by Merrick, who produces the fibre in the presence of benzene which coagulates the acetate fibre.

The Viscose-fibre approaches natural silk in strength and even surpasses it in lustre. It has great attraction for dyes, and for its low conducting power, is used for the insulation of fine electric wires. The acetate silk, owing to its non-inflammable character, has a decided advantage over Chardonnet silk. But the product being expensive at present, it is not much used in the textile and gas-mantle industries.

86. Other Important Technical Applications of Cellulose acetate.—Besides these and many other applications of cellulose acetate, it is being increasingly used in all cases where the inflammable and explosive nature of the nitrates of cellulose is considered objectionable and dangerous; and with the achievement

of the manufacture of cheap acetate, it promises to oust the nitrates from most of their exclusive technological strongholds. Cellulose acetate possesses many of the physical properties of the nitrate of cellulose and would undoubtedly have replaced the nitrate, were it not for the fact that the acetate is somewhat more expensive. Nevertheless some war-uses for cellulose acetate have been found. It is used in the manufacture of a varnish for aeroplanes as it has the property of producing a non-inflammable and waterproof surface. Aeroplanes with transparent wings * are undoubtedly made of some special form of cellulose acetate, probably the form known as cellate. The acetate is also finding a current demand for making special kinds of lacquers; and cellulose acetate sheets are also coming into use in situations where the explosive quality or higher degree of inflammability of the nitrate would be considered unsafe. For this reason, automobile goggles are now being made from cellulose acetate.

It is also gradually replacing the nitrates in the manufacture of celluloid. One quite interesting application of cellulose esters in the manufacture of what is known as the **mother-of-pearls**

---

* Little, Jour. Ind. Eng. Chem., 8, 956 (1916).

should be mentioned.* It has been proposed to manufacture it by adding materials which produce lustre, such as fish-scale tincture, to a solution of cellulose esters; the mixture is then formed into films which are placed in press and shaped into blocks by heat.

.87. Pauly process of making Substitute for Silk.—We now come to the Pauly process of manufacturing artificial silk. The difficulty of filtering a solution of copper hydroxide in aqueous ammonia, known as Schweitzer's reagent, by the usual methods has long been felt by chemists owing to the ready solubility of the filter-paper in this reagent. This fact, as we have seen, has been industrially utilised in the manufacture of artificial boards or planks, Willesden paper, Willesden cloth and Willesden canvas. †

The Pauly or Cupramine process of manufacturing a substitute for silk has successfully developed out of the fact that cellulose goes into solution in ammoniacal copper hydroxide which is prepared on a large scale by passing air through copper turnings in ammonia. The action on cellulose (*q. v.* pp. 103-4) is considered to be a

* Claessen, Eng. Pat., 6893, (1914).

† Vide pp. 103 and 104 of this book.

chemical one.* The cellulose solution is forced through capillaries into a bath of weak solution of an acid; and the fibres so produced are very suitable for textile purposes. The threads have a good silky appearance, the product being called "Glanzstoff" in Germany. The Pauly silk has become a formidable rival of Chardonnet silk in recent years.

88. Further Development of the Industry.—Quite recently artificial silk has been prepared from sea-weed † and thus a neglected source has been tapped to play a rôle in the future history of silk-manufacture. Sarasin has succeeded in making silk from the "slime" of the sea-weed which is thrown up in immense masses on the coasts of Normandy, Norway, Scotland and Canada. An English company is said to be exploiting the process.

89. Correction of the Drawback in Artificial Silk: Comparative value of Silk produced by different processes.—Artificial silk made by the above methods is very much weakened by the action of water. This drawback is, however, greatly removed by plunging the fabric in a bath of aqueous formalde-

* Piest, Die Zellulose, 1910.

† La Nature, Paris *ref.* Scien. Amer. Dec. 5, (1914).

hyde.* The threads are very fine, uniform and continuous. Owing to the ease with which textiles purely made of them tear, they are generally woven with mixed fibres. As regards the price of the silk produced by the various processes, it should be said that the acetate silk which compares favourably with natural silk, is not cheaper than the natural stuff at the present moment. As the industry has attained great significance, it would be convenient to have an idea of the cost of production of the commodity of different makes as well as the price of the natural stuff from the following approximate figures :—

Natural silk	Chardonnet silk
per lb.	per lb.
13*s*. 3*d*.	5*s*. 9*d*.
	Viscose silk
	per lb.
	4*s*. 6*d*.
	Acetate silk
	(almost the same at present as natural silk)
	Pauly silk
	per lb.
	2*s*. 9*d*.

90. Artificial Silk revolutionises the incandescent Mantle-industry.—It

* Beltzer, Zeit. angew. Chem., 21, 1731, (1908.)

has been found in a previous chapter that Welsbach gas-mantles are prepared by impregnating cotton-mantles or stockings with a solution of cerium and thorium nitrates, and by subsequent burning.* Owing, however, to the natural staple of cotton being short and owing to the presence of torsion and hollow lumen in the fibre, small volcanoes burst in the threads, rendering the mantle fragile and useless after some time ; while artificial silk being uniform, solid and continuous, it has been found to be very suitable for mantle-making. Moreover, whilst the artificial fibre is itself ready for impregnation, pure vegetable fibres have first to undergo a laborious and tedious process of purification.

91. Methods of making Gas-mantles from Silk.—In the earlier methods of mantle-making suggestion was made to use Chardonnet silk by adding the Auer mixture † to a solution of cellulose nitrate before squirting it through fine jets. But the method which has finally proved to be successful was heralded by the patents taken out by Plaisetty in 1901 and 1903. ‡ In

* Vide pp. 87-91 of this book.

† *Loc. cit.*

‡ Eng. Pat., 20747, (1901.)
Ger. Pat., 141244, (1903)

the first of these patents greater importance was attached to adding the mixture of cerium and thorium nitrates to the solution of cupramine cellulose, but according to the second which has proved so successful, the Pauly fibre is impregnated with Auer mixture, then dried and burnt as usual. It is remarkable that the solid fibre of the silk should so easily take up the illuminant mixture which is held by the phenomenon called adsorption. After burning, however, the skeleton of oxide on the mantle becomes loose and falls to powder. In order to keep it uniform and permanent, it is subjected to a process of "fixing."

92. Effect of the Substitutes on Natural Silk Industry.—It is evident from what has been said that, with the progress of the artificial silk industry, the cheaper artificial stuff would be increasingly flooding the market, and the already tottering natural silk industry of India would receive correspondingly serious shocks ; and the dying industry may ultimately be altogether extinct. We are afraid, here also a case somewhat parallel to the history of the natural indigo-concern might be rehearsed in no distant future.

Leaving the question of export out of consideration, even for saving the Indian market

from being rigidly captured by the much cheaper foreign artificial silk for the various purposes just reviewed, attention should be directed to the production of this article in India. There is the raw material,—cotton, the production of long staple of which is, however, intimately connected with scientific agriculture. India was formerly the only cotton-producing country and used to supply the world. Now she supplies 3,442,000 bales out of total 22, 500, 000 bales.*

* G. S. Eddy's Statistics, S. C. Mag., Jan., (1916).

CHAPTER XII.

Some "Peace Industries" and Industries for National Defence Based on Cellulose.

93. Chemically treated Cellulose* the basis of numerous "Peace Industries" as well as Explosives.—The action of strong nitric acid on cellulose in the presence of concentrated sulphuric acid gives rise to cellulose nitrates or pyroxylins which form the basis of numerous important industries. It has been seen that the lower nitrates of cellulose have been utilised in developing the Chardonnet silk, and foreshadowed the origin of artificial silk-mantle industry. It will be presently found how the products of the above chemical reaction are extensively utilised in the various "peace industries," as they are called, chief amongst which may be mentioned their earlier application in photography, the present-day cinematograph

---

* Vide also the chapter on "Artificial Silk" including the technical uses of cellulose acetate, p 109.

films and in the manufacture of celluloid, besides the silk and the mantle industries already referred to ; whilst the higher nitrate of cellulose, technically known as gun-cotton, is largely employed in the manufacture of "high explosives". The industrial application of cellulose in these directions will now be briefly described.

94. Collodion : Manufacture of Celluloid Articles.—When cotton is subjected to the action of a warm mixture of nitre and strong sulphuric acid, a mixture of mainly tetra-and penta-nitrates of cellulose is produced. They are dissolved in ether and alcohol, the solution being generally known as collodion.

Collodion is used in surgery for covering wounds over which it leaves a very thin film ; it is extensively used in the manufacture of celluloid, in photography and for making various kinds of lacquers. **Celluloid** is a mixture of collodion-cotton, camphor and other ingredients, producing a material from which imitations of starched linen and ivory are made ; when mixed with a desirable colour, it is used for making numerous decorative objects, such as artificial corals, tortoise-shell and amber. Celluloid is also employed largely in the manufacture of toys, combs, buttons and the Indian *churies* ; besides

these, artificial horse-hair, handles of sticks and umbrellas are also sometimes made of celluloid. These articles are, however, highly inflammable. Quite recently, on account of the non-inflammable character of cellulose acetate, it is gradually replacing the nitrates in the manufacture of celluloid to some extent.

95. Collodion in the Development of Photography and Cinema.—Collodion has also proved to be of great service in developing the art of photography. The different phases of photographic development, from the troublesome wet collodion-process to the modern dry plate system, reaching a form of perfection in cinematograph for exhibiting animated pictures, consist of an interesting history of continual attempts at a judicious application of starch and cellulose in some form or other. Collodion film was first introduced by Eastman in the year 1887; and with the invention of photographic film, the art of snapshotting began to attain a prominent position. The collodion fims are, however, a source of great danger, especially in the exhibition of pictures by the cinematograph process.* This is due to the fact that the

* The disastrous fire which broke out at Paris in May, 1897, killed 132 spectators.

extremely inflammable film has to be passed by rapid jerks between the intense heat of the electric arc-light and magnifying lens. If such films remain stationary only for a fraction of a second at a time, it may lead to dangerous conflagration.

96. Application of Collodion in Leather-finishing and Lacquer-making. —In recent years collodion solution is finding technical application in leather-finishing in producing enamels for leather * and in manufacturing lacquers. Various kinds of metal-lacquers as well as brush, dip or spray lacquers, as they may be classified according to the method by which they are applied for producing a matt, satin or glossy surface, are made from collodion. These lacquers contain resin and are thus defined by Worden †: "Resin lacquers are solutions of gum-resins or resins in fusel oil and pyroxylin solvents without linseed or other drying oils, and hence are not varnishes."

It is thus observed in how many different directions chemically treated cellulose has found technical applications which may be termed

* Higgins, Leather Trades Year-Book, 148, (1914); Jour. Soc. Chem. Ind., 53, 704; Callan, Leather World, 4, 523.

† Worden, Nitro-cellulose Industry, Vol. I, 305, (1911).

their "peace uses" ; and we now proceed to briefly mention the industries for national defence based on that substance.

97. Gun-cotton : its Application in the Manufacture of "High Explosives." —When purified cotton, cotton-waste or, more recently, cellulosic pulp is dipped in a bath of one part of nitric acid and two parts of sulphuric acid for 4-10 minutes below 10°C, then removed and carefully washed free from acid, it is converted into what is called gun-cotton which is hexa-nitrate of cellulose.* It is insoluble in alcohol and ether, mixed or separate, but forms a syrupy solution with acetone,—a property on which depends the "high explosives" industry based on cellulose. Gun-cotton preserves the fibrous nature of cotton, burns very energetically and explodes with tremendous violence on percussion. Gun-cotton was discovered by Schönbein in 1846 ; its explosive property and method of manufacture were subsequently studied by Lenk (1850-53) and Abel (1865). The cotton used in its manufacture is generally

* Ber., 13, 186.

† "Cotton-waste" of India which used to be exported to Germany prior to the war (1914), is now being utilised for making coarse cloth in Bombay.

the "waste" from cotton-spinning †, and more recently, purified pulp has come into use.

Cellulose hexa-nitrate, as it is chemically called, is insoluble in water, alcohol and ether. When not completely washed free from all traces of acid, it is liable to undergo spontaneous decomposition and sudden explosion. It goes into a somewhat syrupy solution in acetone which, with nitro-glycerine, is used in making the most powerfully explosive maximite or cordite; when mixed with other ingredients it is used in making nitro-gelatine or blasting gelatine, and forcite. Gun-cotton as well as collodion are extensively used for manufacturing varieties of high grade "smokeless powders" which are used for military purposes. They are conveniently used in cartridges, but are considered expensive for blasting and mining work. It is important to note that acetone is extensively used in the manufacture of these explosives.

Combined nitrogen is thus found to be an essential constituent of most explosives which may either be mechanical mixtures as for instance gun-powder, or chemical compounds as in the case of gun-cotton, nitro-glycerine and picrates etc. It is extremely striking to observe why nitrogenous compounds, mixed or individual,

come to display the highly explosive property. It is particularly interesting that innocent cellulose when in chemical wedlock with nitrogen becomes such a formidable engine of destruction.

A discussion of the constitution of explosives is, however, not within the scope of the present work; and we now proceed to see how cellulosic material has been directly or indirectly influencing quite a large number of other important industries in unexpected directions at the present day.

CHAPTER XIII.

*Fermentation and Distillation of Wood and Wood-waste : * Manufacture of Chemical Food.*

When studying the subject of the chemical industry of starch, it has been found that starchy material is largely used in the manufacture of alcohols and acetone. In recent years cellulosic substance in the shape of wood, wood-waste such as saw-dust and waste liquors from the chemical pulp industry have also been successfully employed in the production of lower and higher alcohols and acetone. The seed of the possibility of fermenting cellulose lay, however, in the observation of Braconnot, who found as early as 1819, that prolonged digestion with sulphuric acid converted cellulose into reducing and fermentable sugar, so that alcohol and its numerous derivatives might be made from

* Reference should be made to pp. 96-101 in this connection.

sawdust and rags which have genetic relationship with the fermentable carbohydrates.

98. Manufacture of Alcohol by Fermentation of Wood and Wood-waste.—For nearly hundred years chemists have endeavoured to develop this observation into a commercial success. Attempts at commercial operation* of the Simonsen process (1889) in Sweden and the Classen processes (1900-03) in Germany presented fresh practical obstacles and led to their abandonment. It remained for Ewen and Tomlinson to overcome the fundamental technical difficulties underlying all these attempts and to put forward the first process capable of producing ethyl alcohol from wood on a large scale. In this process about 25 per cent of the wood is converted into fermentable sugars. The Ewen-Tomlinson process consists essentially in taking saw-dust or wood-waste and spreading it over with dilute sulphuric acid. The charge is preferably put in a rotary digester or converter which has a protective and heat-insulating lining, and is quickly brought up to the critical temperature; the reaction is then extremely rapid, if not instantaneous. The cooked cellulosic matter is now extracted with water; the acid extract is neutralised with lime; and

when calcium sulphate settles down, the liquor which contains the fermentable sugars, is treated almost as precisely as molasses, using special ferments. * It has also been proposed to manufacture alcohol and acetone from the sugars by the action of *bacillus macerans.*

99. Industrial Alcohol.—The problem of industrial alcohol (*q. v.* pp. 60–61) engages the attention of chemists at the present day. Amongst the uses of waste sulphite, sulphate and soda liquors, † their application to the production of alcohol is important. In addition to the numerous industrial applications of alcohol as a solvent and for the manufacture of chemicals, there is a growing demand for it as a heating agent in special cases. It is coming into use as a fuel primarily in the internal combustion-engines and it promises, in no distant future, to replace gasolene in automobiles, at any rate in the pleasure-cars. After the introduction of solid alcohol, the so-called "Steero," it has come to be

---

* Little, Utilisation of Wood-waste, 104, (1916).

Eckström, Fermentable Sugar or Alcohol from Cellulose-material, Swed. Pat., 41159, (1916).

† Vide pp. 97,98 and 100-101 of this book.

Kressmann, Manufacture of Ethyl Alcohol from Wood-waste, Jour. Ind. Eng. Chem., Nov., (1915).

widely used in the United States with much convenience. The price of industrial alcohol roughly at 1s. 4*d*. per gallon which is believed to be well within the range of vision* in that country, may ensure its commercial success as a fuel.

100. Hardwood Distillation Industry: Methyl Alcohol, Acetic acid and Acetone.—Besides these fermentation-industries based on cellulosic material, the distillation of hardwood † is an industry of great significance. It yields inflammable gas, methyl alcohol, acetic acid, acetone and wood-tar. There is a number of methods, but dry distillation with lime is the one in general use. Owing however to the greater demand for acetone which is extensively consumed in the manufacture of smokeless powders and cordite etc., it has been attempted to convert the acetic acid to acetone. And it has been recently found that acetic acid even when dilute in the form of pyroligneous

---

* Little, Industrial Alcohol, Acetone and Acetic acid, Jour. Ind. Eng. Chem., 954, (1916).

† Klar, Modern Distillation of Wood, Jour. Soc. Chem. Ind., 667 and 722, (1897).

Katzenstein, Contributions of the Chemists to the Hardwood Distillation Industry, Jour. Ind. Eng. Chem., Nov., (1915); Withrow, *ibid.*

acid, can be easily converted into acetone by passing its vapour through a tube or a chamber heated to about 500°C, over a catalyzer consisting of pumice stone with barium carbonate ; the yield is satisfactory and the process continuous.* It is therefore evident that the products of fermentation and distillation of cellulose bring it on a line parallel with those products obtained from the fermentation of starch.† So starch and cellulose are alike essential to the stability and successful development of numerous sister-industries.

101. Wood-tar and its uses.—Before dismissing the subject of the destructive distillation of wood, mention should be made of wood-tar, the disposal of which was at one time a source of great trouble to the wood-distillers. Now the name *tar* at once recalls to our mind myriads of beautiful and charming dyes discovered by the synthetic chemist, for the vast commercial manufacture of which, however, the richer source of coal-tar has been so successfully tackled. Wood-tar which has only a limited supply has also proved to be of technical value.

---

* Squible, Jour. Am. Chem. Soc., 17, 187, (1895).

† Vide pp. 55-61 and 68-69 of this book.

When it is distilled, it yields below 150°C a distillate called "light oil" and between 150°—250°C a second crop known as "heavy oil." The light oil is used as a substitute for the oil of turpentine in making paints and varnishes, whilst the heavy oil is worked for, among others, wood-tar creosote. When the distillation is stopped at 250°C, a viscous, brownish liquid is obtained which is used in making shoe-maker's wax, axle-grease and for giving an impervious coating inside casks and barrels. Wood-tar as such is also used in tarring ropes and nets, in ship-calking and as a preservative of timber.

102. Manufacture of Food from Wood-cellulose.—As starchy material is used as animal food, attempts have also been made to reduce cellulose to some suitable form fit for human consumption, and such a conversion is anticipated as possible from the genetic chemical relationship of the two classes of carbohydrates. Little has devised a process for making carbohydrate cattle-feed by treating cellulosic material with hydrochloric acid. The problem, however, of manufacturing some sort of cheap chemical food has long been looming in the mind of the imaginative chemists. But such problems are actively taken up in times of acute emergencies

when the question of food-supply becomes extremely vital ; and it is quite recently that Haberlandt has made some practical pronouncement on what may be termed an "auxilliary diet" before the Prussian Academy of Sciences. * This new food may properly be called "wood-flour" and consists of a mixture of finely ground sap-wood and fodder of domestic animals in certain proportions. Sap-wood dust can be used in certain circumstances as fodder for animals, and even, in case of necessity, as human food. Living white sap-wood of many trees contains carbohydrates of nutritive value to extent of 20—25 per cent., while the dead heart-wood is practically destitute of nutritive substances. In selecting the tree care should be taken to reject those which contain bitter or injurious principles. Although the manufacture of this food does not involve any chemical process, it is undoubtedly true that knowledge of chemistry and chemical researches have opened up this new line of application of cellulosic material.

The potential food materials are, however, enclosed for the most part in cells which have become lignified or woody. In the alimentary

* Nature vissenschaften, April 9, (1915).

canal of animals, especially that of the cud-chewers, most of the cell-walls of plants which consist of pure cellulose, are dissolved ; in the human alimentary canal, however, it is only the walls of the tender cells which are dissolved. But neither man nor animal can dissolve the lignified cell-walls. If, therefore, the food-content of the lignified cells in wood are to be made available, it is primarily necessary to grind the wood fine enough in order to break down the walls of the individual cells ; and for this purpose grinding should be sufficiently energetic to reduce wood to fine powder. It is then that the digestive fluids of the alimentary canal can easily reach the contents of the cells.

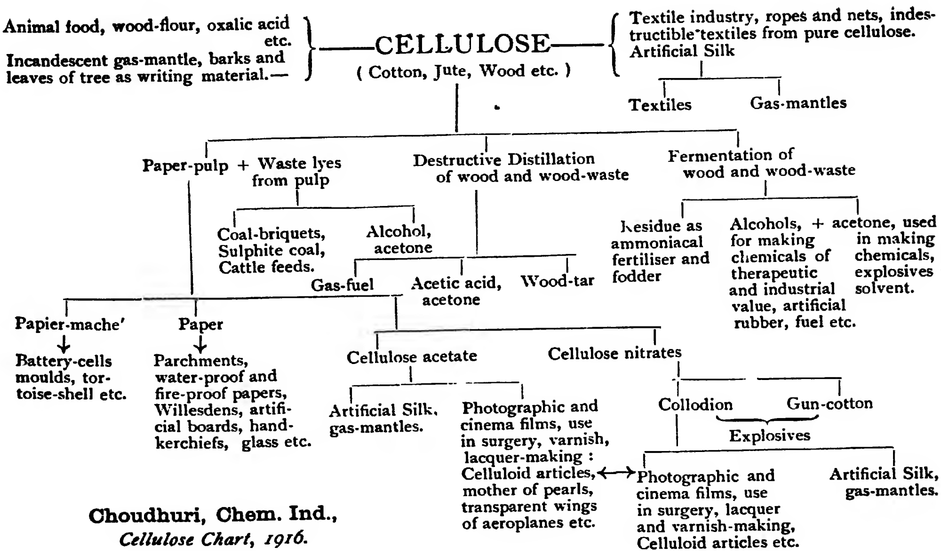
103. Wide Scope of Starch and Cellulose in Chemical Technology.—We have thus found in these pages how extensive and varied are the uses of starch and cellulose in the arts and industries. The number of the vastly different organo-chemical industries which are directly based upon these two materials or are influenced by them is overwhelming. The numerous channels in which they are finding application in the light of recent researches day by day, cover a very wide field in the domain of the techno-chemical world. The following

chart will briefly show the numerous industrial applications of cellulose and will indicate the points where they come on the same level with similar starch-industries as outlined in the starch-chart.

We here drop the subject of the modern industries based on starch and cellulose, and pass on to a consideration of the present position and the recent advances in miscellaneous industries apertaining to the Indian vegetable kingdom.

---

* Vide page 73 of this book.



Choudhuri, Chem. Ind.,
Cellulose Chart, 1916.

CHAPTER XIV.

Recent Advances in Miscellaneous Organo-chemical Industries in India : Industrial Potentialities of India.

The extensive region of forest in India offers splendid and vast quantities of raw-material for a very large number of important industries and bye-industries. We may mention pulp-manufacture, fermentation of wood and wood-waste for alcohols, the destructive distillation industry, the explosives industry, artificial silk from wood-pulp and cotton, match-making, tannin-extraction, and manufacture of resins and turpentine; besides these, there are some important species of forest-grass which yield oils of commercial and industrial importance. It is evident that the products from each of the principal industries are the bases of a huge number of chemical industries, ranging over almost the whole of organo-chemical technology. In recent years, attempts are being made, in certain directions, to develop

the forest-industries in India,—a country of which no less than quarter of a million square miles is covered with forest; and it is interesting to note the lines of progress recently recorded. *

104. Manufacture of Paper-pulp.—As regards pulp-making, promising beginning has been made. The Tittaguhr Paper Mills in Bengal have successfully made bamboo-pulps on a commercial scale; and concession for the extraction of bamboo has been granted to some firms in Bengal and Burma. Some arrangement has also been made to get materials from the Kulu forest in the Punjab for the manufacture of wood-pulp. In the United Provinces and Assam suitable grasses are available in enormous quantities from which an important industry of grass-pulp may spring up in future, and *sabhai* grass has already been utilised in this direction.

105. Prospects of Tannin-industry.—The attention of Government has, for some years past, been drawn to the extraction of tannins, especially from the bark of mangroves which largely grow in Burma, and the services of an

* Kershaw, Quinquennial Report of the Forest Administration in India, 1915.

expert have been secured to tap this source. The Indian forests along the Himalayas, in the Central Provinces and Burma abound in trees rich in valuable tanning materials. If a good quality of the substance can be profitably extracted, a commercial success in this direction is expected in near future.

106. Present State and Prospect of Resin, Oil of Turpentine, Essential Oil, Cinnamic acid and other miscellaneous industries.—Another important industry related to the Indian vegetable kingdom is the manufacture of resin and oil of turpentine in which some definite progress is being made. The pines in the Himalaya-regions are rich in resin and turpentine. The present writer in course of his journey through the forests of the Buxa Division, an eastern section of the Himalayas, found fine specimens of resin with good flavour as exudation from the body of trees. Cutch is also a resiniferous substance manufactured in many centres all over India by boiling chips of *khair* wood,—a product which commands a large internal trade. The fragrant balsam known as Nan-ta-yôk or Burmese storax which exudes as a honeylike matter from bark of trees in Burma and Assam, deserves special

mention. It has been in use as an incense and for medicinal purposes from very ancient times. It yields about 6 per cent essential oil and 53—54 per cent pure resin which is rich in cinnamic acid ester. The balsam is a valuable perfume and is a rich natural source of cinnamic acid.* In the Punjab and the United Provinces distilleries have already been established which are now turning out substantial quantities of resin and turpentine; they are used in the manufacture of paper to some extent, and largely of paints and varnishes; they have immediate possibilities of being employed in making lacquers. The Indian demand has already affected the import of these commodities from other countries.

It is important to point out in this connection that pinene and allied unsaturated hydrocarbons which have significant bearing on a number of industries are the constituents of the oil of turpentine. Consequently industrial researches on rubber-synthesis, artificial camphor † and essential oils including ionone and others will receive great impetus, if requisite quantity of cheap terpenes (pinene) be placed

---

* Hooper, Agric. Ledge., Veget. Prod. Ser. 84, (1904).

† Jour. Soc. Chem. Ind., 75, 881, (1904); 249, 857, 902, 1188, (1905).

at the disposal of the chemist in the technological institutes (*q. v.* p. 42, foot-note) or factories. It is hoped that the successful turpentine industry may therefore be fraught with great chemico-technological issues in future.

Quite recently, however, some indegenous preparations of sodium salicylate, salicylic acid and aspirin have all been made in the laboratory* from the oil of winter-green (methyl salicylate) obained by distilling leaves of *Gaultheria Fragrantissima* which grows in the forest of Assam. Some practical attempt is being made at the present moment to develop the destructive distillation industry in the Deccan where the manufacture of santal oil is already a standing industry.

107. The Agar Industry.—The trade in agar-wood and the preparation of essential oil from it deserve mention. The eagle or aloe-wood tree which grows in Assam, Burma and Tipperah (Bengal) is very valuable. The bark of this tree is made into *sachi* paper (*q. v.* p.93). Inside this wood run dark-coloured parallel veins, loaded with odoriferous resinous matter. The agar has been in use from ancient times all

* Singh, Triennial Forest Conference, Dehra, 1916.

over the East as perfume, medicine and incense. The high value of the stuff will be evident from the fact that, at one time, it was sold by weight against gold and silver, and a Rájá of Assam used to pay his tribute to a Mahomedan Governor in this substance. It is remarkable that pure *attar of agar* which is a highly valuable essential oil is made, even at the present day, by a quite indegenous method of steam distillation, at the villages of Srinagar and Rajinagar in Karimganj (Assam).

Besides these uses of *aguru*, as it is called in Sanskrit, the wood itself is also of technical value. For its odoriferous nature, it is an important ingredient in making the *agar-bátis* or lights in Bombay. It is used for making beads, rosaries and crucifixes, and forms an efficient component of a mixture for embalming the dead. It is used in burning the dead bodies of the *Bráhmins* and notable persons of other classes as a mark of honour. The wood as powder also finds various interesting medicinal applications.*

108. Rubber, Alkaloid and Tea industries.—It may not be out of place to

* Hooper, Agric. Ledg., Veget. Prod. Ser. 78, (1904).

mention in connection with Indian vegetable produces that rubber and alkaloid are important standing industries, the latter being exclusively under Government management. The rubber-plantations are extensive in Assam, Burma and the Straits Settlements, while cinchona plants from the barks of which quinine, cinchonine and cinchonidine are extracted, are largely grown chiefly in the Darjeeling side of Bengal, the Deccan and Burma; while the opium-alkaloid industries and the world-famous indigo-concerns exist chiefly in Behar and the United Provinces. It is necessary to note that tea which is a very important produce of the Indian soil, cannot be included in the category of chemical technology, as tea-leaves are not required to be subjected to any chemical process in order to render them fit for human consumption.

109. Prospect of Preserved Vegetable Foods.—Another interesting phase of Indian industry bordering on scientific technology deserves special reference. The manufacture of preserved vegetable foods which is making remarkable progress in the Western countries and in the Far East * in recent years, seems to

* Shriver, Canned Goods Trade in the Far East, Special A. S, 92, Dept. Comm., U. S. A.

have good prospects in India, the tropical fertile soil of which produces many delicious and fine varieties of fruits and vegetables. * The importance of this industry is great in normal conditions for expeditions, voyages and tours as well as in times of war. The successful development of the canning industry which has rendered the flow and use on the table of the finest produces of different countries in all climates and corners of the world, is a signal instance of the intimate co-operation of chemistry, bacteriology and agriculture. Promising start along up-to-date scientific methods has, however, been made in some best fruit-growing localities mainly for canning mangoes † and pineapples which are extensively produced in India. Some minor fruits of the Indian soil are also of industrial value and tamarind may be cited as an instance. It is largely consumed as a favourite ingredient in curries, chutnies and sauces, and is exported in bulk for medicinal purpose under the name of East Indian tamarind. ‡ It is from Indian tamarind that a palatable variety of

* Chaudhuri, Jour. Ind. Eng. Chem., 8, 618, (1916) ; C. A., 10, 2252, (1916) ; Sci. Amer., Aug., 126, (1916).

† Chaudhuri, *loc. cit.*

‡ Hooper, Agric. Ledg., Veget. Prod. Ser., 101, (1907).

tamarind syrup is made in America which has found a good market in Italy. The tamarind seed which contains 63-64 per cent of starch is also not without value. It is applied as a medicine in many forms according to Ayurvedic and Yunani systems of treatment of disease. It is also used as a famine food * and a size (*q. v.* pp. 51-52).

Conclusion

119. Vast Industrial Potentiality of India.—This brief summary will serve to give some idea of the huge vegetable wealth of India so rich in her vast stores of neglected raw materials suitable for establishing organo-chemicall industries, both on big and humble scales. The extensive industrial potentiality of India is realised from the varied nature of the numerous industries referred to in this volume, which are directly or indirectly dependent on starch and cellulose. It has been found that India is supremely rich in these produces which is borne out by her export of these raw commodities for application in the arts and industries of

* Paton and Dunlop, *ibid.*, 84, (1904); Hooper, *loc. cit.*

other countries, and also by her huge neglected resources.

120. Factors Essential to the Industrial Advancement of the Country.—It is clearly witnessed that the industrial nations of the world are continously surging upon India with their manufactures and are rigidly capturing its market ; the weak indegenous industries unable to stand competition are faltering by wayside and giving them free pass ; many excellent industries succumbed in the past, and the yet-struggling ones are threatened with hopeless collapse. For the advancement of Indian industrial interests, for the revival of the dying Indian industries, for the development of the weak and nascent industries and for the establishment of new ones, co-operation between sound businessman, industrially scientific man and Government is most essential.* Here, in India as elsewhere, protective tariffs for the defence and expansion of the infant industries,† facility for sale

* In this connection it is important to read the admirable and suggestive presidential address before the Chemical Society by W. H. Perkin on "The Present Position of Organic Chemical Industry (in England)," Trans. Chem. Soc, 557, (1915.)

† Marshal, Memorandum on the Fiscal Policy of International Trade, 1908 ; *Cf.* also the comment of the *Times* (London) :

of indigenous products through Government stores and agencies, granting of machineries on hire-purchase system, banking facility for granting long-term industrial loans at a low interest, reduced rate of railway freight for carriage of materials for manufacturing purposes, and giving expert commercial information and advice whenever needed, are essential to the betterment of the industrial position. These matters which although do not directly come within the province of our present subject, are factors with which the industrial uplift of India is closely bound up.

In, all industrial organisations, however, able scientific brains should be at the head of affairs; and chemists must not only thoroughly master the technique of the existing manufacturing processes, but also constantly grasp details and improve upon them by researches, so that a mother industry may successfully branch out into a number of economic bye-industries which are harmoniously dovetailed into one another in

"How would," says the *Times*, "education have enriched Germany materially, if her industries had been left to cope *unaided* with the mature industries of England? From what has improved food come but from the wealth gained by the protected nascent industries? Education and improved food have, no doubt, made very excellent use of protection. But the first was practically powerless and the second non-existent, until the nascent industries were fostered by being shielded from the crushing competition of English mature industries."

course of their development. The old-fashioned rule-of-thumb principle of work cannot ensure stable success in the long run and far less effect expansion ; nor are industrial concerns matters for amateurs and pure academicians. To secure permanence and expansion of an industrial organisation, intimate co-operation between Science and Industry is of vital importance. If experts and scientists are relegated to the background, the business is destined to come to grief.

We may only conclude by hoping that it is not impossible to look with confidence to a near date when the Indian capitalists will come forward to make investments in industrial enterprises and technical researches, and educated Indians will come to co-operate with the willing capitalists and the Government, so that India may take her part in the scientific and commercial activities of the world. The Government have been trying to substantially help the people in this direction ; the people are also gradually becoming conscious of the vast industrial potentialities of the country, and humble activities are happily visible in response to this natural pulsation.

THE END.

INDEX

Name of person is given in italics.

Figures refer to pages.

D

E

F

T

U

V

W

X

Z